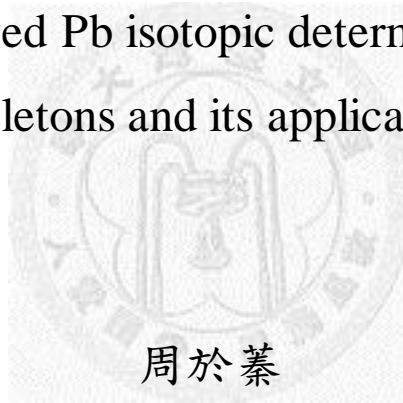國立臺灣大學理學院地質科學研究所

碩士論文

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珊瑚骨骼中月解析度鉛同位素測量及其應用

Monthly-resolved Pb isotopic determination in coral
skeletons and its application

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摘要

珊瑚骨骼中的微量元素與同位素分析，可作為地質科學、古海洋學、大氣科學與環境科學研究的有利工具。其中，鉛同位素訊號，可用來重建海洋與大氣中的鉛通量，計算出地區性甚至全球性的鉛傳輸系統模型。但是，受限於低鉛含量 (10s-100s ng/g)，在過去研究，鉛同位素紀錄僅能被應用於多年至十年尺度之水文變化與人為污染的研究議題上。

此研究精進化學分析步驟與儀器測量方法，建立多頻道感應耦合電漿質譜儀 (MC-ICP-MS, Thermo Electron NEPTUNE) 之高精度皮克級鉛同位素(^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb)分析。離子交換樹脂分離方法可從低鉛含量樣本中萃取出 90% 以上的鉛，化學空白值僅 2 ± 3 pg。重複分析 300s-1000s pg 的國際鉛標準品，精準度可達 $\pm$ 2‰ (2σ)；此分析量相當於 5-10 mg 的珊瑚樣本，也就是說，現在我們可以測量月解析度的珊瑚鉛同位素變化紀錄。

本研究分析了一株採自越南中部 Son Tra Island (16°12'59.4", 108°1'57.1")的微孔珊瑚。1978-1982 年間的鉛濃度變化由 35 至 70 ppb；鉛同位素資料範圍為：^{208}Pb/^{207}Pb = 2.4262-2.4813，^{206}Pb/^{207}Pb = 1.1226-1.1745。在時間序列上展現的特性如下：(1) 鉛同位素顯示出明顯的季節性變化。 (2) 季節性的鉛同位素變化指出兩個主要的來源端成份在乾季與濕季的不同混合結果，分別為河流沉積物與鄰近開放海域的海水。 (3) 鉛濃度紀錄呈現年間逐步上升的趨勢。 (4) 1980 年夏秋期間的 ^{208}Pb/^{207}Pb 和 ^{206}Pb/^{207}Pb 紀錄出現異常低值，推測為亞洲夏季季風和颱風

過後之西南氣流引進馬來西亞、印尼與泰國之氣溶膠，致使鉛同位素比值大幅降低。研究結果證明月解析的鉛濃度變化與鉛同位素紀錄可作為環境指標與來源示蹤劑，幫助我們了解歷史中人為活動造成的影響，過去自然水文變化及特殊事件的發生，更可作為未來永續發展政策的參考。

關鍵字：鉛、鉛同位素、多頻道感應耦合電漿質譜儀、珊瑚、越南中部

Abstract

Pb concentrations and isotopic compositions in coral skeletons have been used to understand the annual to decadal trends of natural hydrological evolution, ocean circulation, and anthropogenic pollution. However, the low Pb content in coral skeletons, commonly of 10s-100s ng/g, has hindered determination of monthly variation of the coral Pb isotopic compositions. Consequently, the applications of Pb isotopic study have been limited.

In this study, the chemical separation of Pb and instrumental technique were improved. A reliable procedure was developed for measuring the isotopic compositions (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb) of pictogram Pb in coral skeletons. The isotopic analysis was conducted on a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS), Thermo Electron NEPTUNE. The overall procedural Pb blank was only 2 ± 3 pg. Replicate measurements on a standard NIST SRM 981 showed that a precision of ± 2‰ (2σ) with 300-1000s pg of Pb could be achieved. This quantity is equivalent to 5-10 mg of coral sample. A sample size of 1.5 ng of Pb is recommended for routine analysis with acceptable external precision.

The monthly-resolution Pb isotopic records during 1978-1982 of a coral *Porites* from the Son Tra Island, central Vietnam (16°12'59.4", 108°1'57.1") were reconstructed. The Pb concentrations vary from 35 to 70 ppb. The Pb isotopic ratios

are 2.4262-2.4813 for $^{208}Pb/^{207}Pb$, and 1.1226-1.1745 for $^{206}Pb/^{207}Pb$. The results yield

the following important points: (1) A clear seasonal-to-annual variation in monthly Pb

isotopic composition was observed; which had never been reported in the literature. (2)

The isotopic compositions $^{208}Pb/^{207}Pb$ vs. $^{206}Pb/^{207}Pb$ ratios suggest a mixing between

fluvial sediments and adjacent open-ocean seawater from the South China Sea. (3) The

Pb concentrations time series shows an interannual gradual increasing trend from 1978

to 1982. (4) The anomalously low $^{208}Pb/^{207}Pb$ (2.426-2.433) and $^{206}Pb/^{207}Pb$

(1.122-1.128) ratios in the summer and autumn of 1980 could be due to the

contribution of aerosols from Malaysia, Indonesia and Thailand. The aerosols were

likely delivered by the Asian summer monsoon and southwesterly flow after typhoon.

The present study indicates that monthly resolved coral Pb isotopic sequence can be

used as a proxy and tracer for the monthly-seasonal environmental change and the

impact of anthropogenic perturbation. The coral Pb isotopic records may help

understand the nature of regional hydrological dynamics, planning of resource

management, and making of sustainability policy.

Keywords: Pb, lead isotopes, MC-ICP-MS, coral, central Vietnam

誌 謝

我的碩士班生涯終於將告以段落，回憶實驗室時光與論文撰寫期間的點點滴滴，百般滋味湧上心頭，曾經，在取樣室中睜著疲憊的雙眼，秤量僅僅幾毫克的珊瑚，不知不覺來到凌晨四點；曾經，在無塵室中與王水、鹽酸、硝酸等渡過二十幾個小時，擔憂自己化學中毒；曾經，連續十來天，每天只睡兩三個小時，陪伴樣本們與海王星女神，在精神、體力上瀕臨極限；曾經，在第二十四個生日面對電腦絞盡腦汁地寫巨集指令處理數據，思考該如何解釋我的實驗結果，難以細數的這些曾經導引出我的 New Life 和 New Status，各面向的壓力與情緒的波折使我的身心都獲得了成長。

過去這段日子，很幸運地受到許多人的照顧，首先要感謝沈川洲老師，其引導與鼓勵，給予我研究的方向與信心，責任制的實驗室風氣也讓我有很多自己的空間去思考，兩肋插刀、不厭其煩地修改我的論文更是令我懷抱無限感激。感謝魏國彥老師、李紅春老師、米泓生老師、學長姐和訪問學者們在 PPP Meeting 中給予的意見與指點。感謝口試委員江博明老師、許世傑老師和林立虹老師對於論文的補充與指正，讓這本論文更加充實完善。感謝瀞之學姊和羅允杰學長在過程中給予很多實驗方面和儀器方面的指導。感謝佩萱時常情義相挺，陪我渡過儀器時間，幫忙部分實驗，也讓我通宵時依然有地方能盥洗。感謝莉容、忠哲、育維、惠媛、君艾、秀秀、韻嫆、韻如、小耿、晉平、皓正、建儒、林可、怡綺、宏偉、羅立、智凱、小四、皓揚、賢元等所有朋友們這一路的陪伴，因為有你們，所以

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我的研究生活才能滿溢溫暖與歡笑。也感謝那個特別的你，在爆炸般的生活中為我分憂，在和暖微風吹拂著的醉月湖畔樹屋上，與我分享故事，一起仰望著即使有光害也依然絢麗的星空。

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Chapter 1 Introduction

1.1   Nature of Pb

Lead is a transitional element with symbol **Pb** (Latin: *plumbum*). Lead has

the atomic number 82 and its standard atomic mass is 207.2 amu. Lead

compounds, PbS, $PbCO_3$ and $PbSO_4$, exist naturally in the continental crust in

rocks and soil. It is usually found in ore with zinc, silver and copper, and is

extracted together with these metals.

Natural lead includes four stable isotopes (Figure 1.1): ^{204}Pb (1.48%),

^{206}Pb (23.6%), ^{207}Pb (22.6%), and ^{208}Pb (52.3%). The three radiogenic isotopes,

^{206}Pb, ^{207}Pb and ^{208}Pb, are products from radioactive decay of ^{238}U, ^{235}U and

^{232}Th, respectively, ^{204}Pb is the only primordial stable isotope with a constant

abundance on Earth in time (Table 1.1).
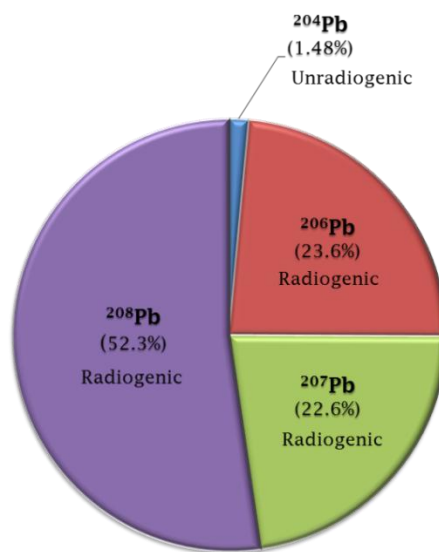
Figure 1.1 Natural lead stable isotope abundance.

Table 1.1 Pb isotopes and half-lives of the decay processes (modified from Komáreka et al., 2008).

Pb isotope	Decay process	Half-lives of the parents (years)
^{204}Pb	—	—
^{206}Pb	$^{238}\text{U} \rightarrow 8\alpha + 6\beta^- + {}^{206}\text{Pb}$	4.466×10^9
^{207}Pb	$^{235}\text{U} \rightarrow 7\alpha + 4\beta^- + {}^{207}\text{Pb}$	7.040×10^8
^{208}Pb	$^{232}\text{Th} \rightarrow 6\alpha + 4\beta^- + {}^{208}\text{Pb}$	1.401×10^{10}

Since the era of the Roman Empire, lead has commonly been used for thousands of years because it is widespread and easy to work with. Lead is transported to natural environment through different pathways, including manufacturing process (e.g., mining and smelting), living use (e.g., batteries, pigments, ceramics, plastics), recycling, disposal of Pb compounds, combustion of fossil fuels (e.g., coal, use of leaded gasoline), and mineral fertilizers and sewage sludge application (Komáreka et al., 2008). During the 20th century, most environmental Pb was attributed to emerging industrial activities. Especially in 1940s-1970s, the combustion of leaded gasoline quickly increased the relative contribution of anthropogenic Pb. (Figure 1.2; Shen and Boyle, 1987; Inoue and Tanimizu, 2008).
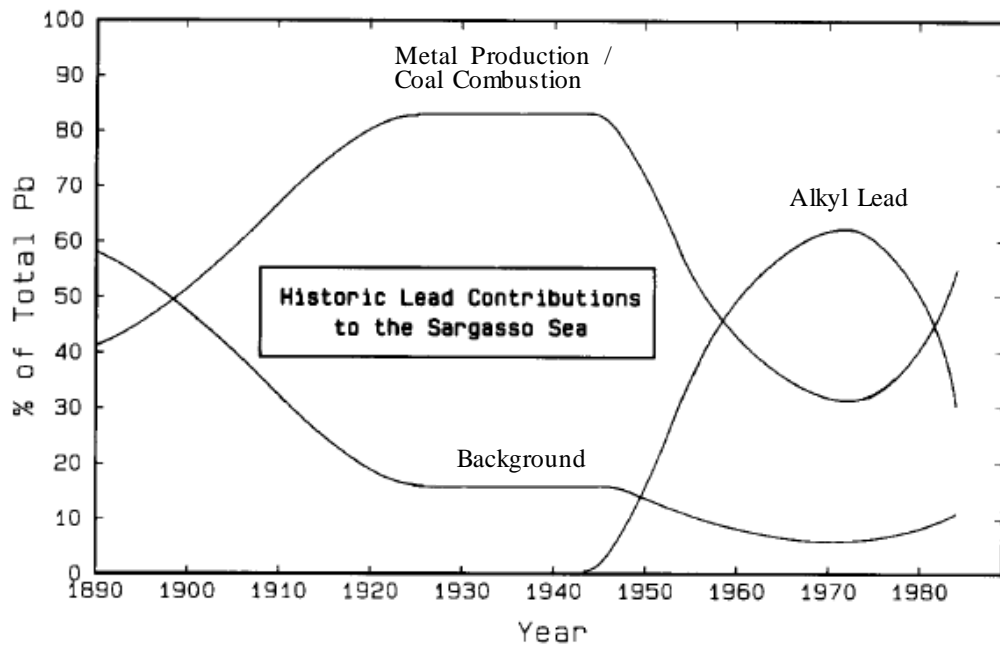
Figure 1.2 Coral-inferred contributions of natural and anthropogenic Pb to the Sargasso

Sea (Shen and Boyle, 1987).

1.2   Application of Pb isotope ratio

Interest in the isotopic composition of Pb in environmental system was raised by attempts to date the age of Earth by Pb-Pb methods (Dickin, 1997). Variations in the relative abundances of Pb isotopes have been demonstrated to be effective tracers for investigating the functioning of natural systems and proxies in different environmental compartments, such as global ore distribution (Figure 1.3; Bollhöfer and Rosman, 2001a), aerosols (Figure 1.4; Millot et al, 2004), air-mass trajectory (Figure 1.5; Hsu et al., 2006), and coral-inferred anthropogenic pollutions (Figure 1.6; Inoue and Tanimizu, 2008).
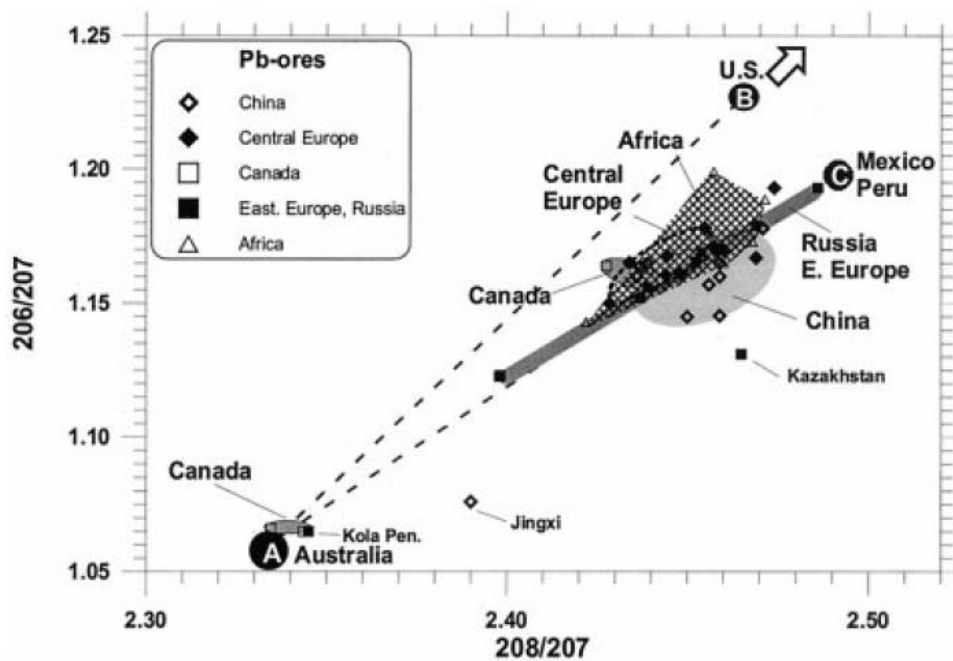
Figure 1.3 Pb isotopic compositions of global Pb ores (Bollhöfer and Rosman, 2001a).
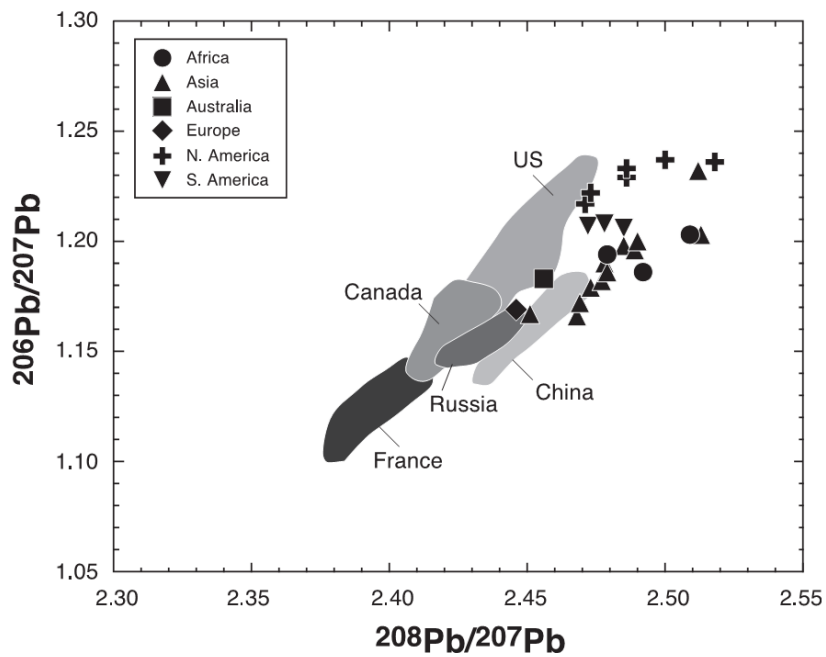
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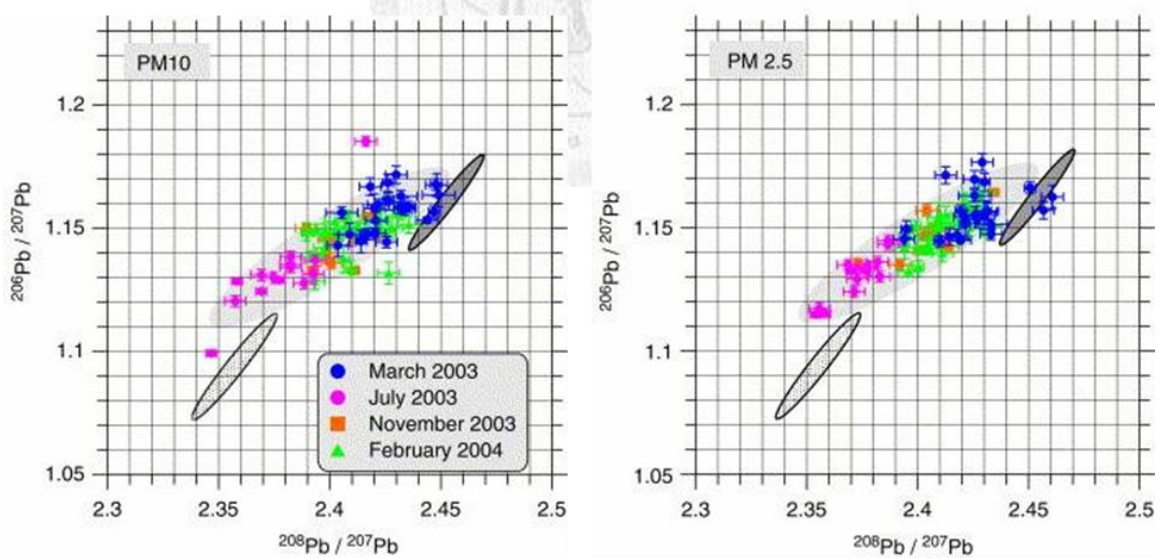
Figure 1.5 Pb isotopic compositions of aerosols in Taipei, Taiwan (color symbols). The
dark- gray area represents the characteristic isotope ratios for the Chinese
aerosols and the dotted area for the Australian aerosols (Hsu et al., 2006).
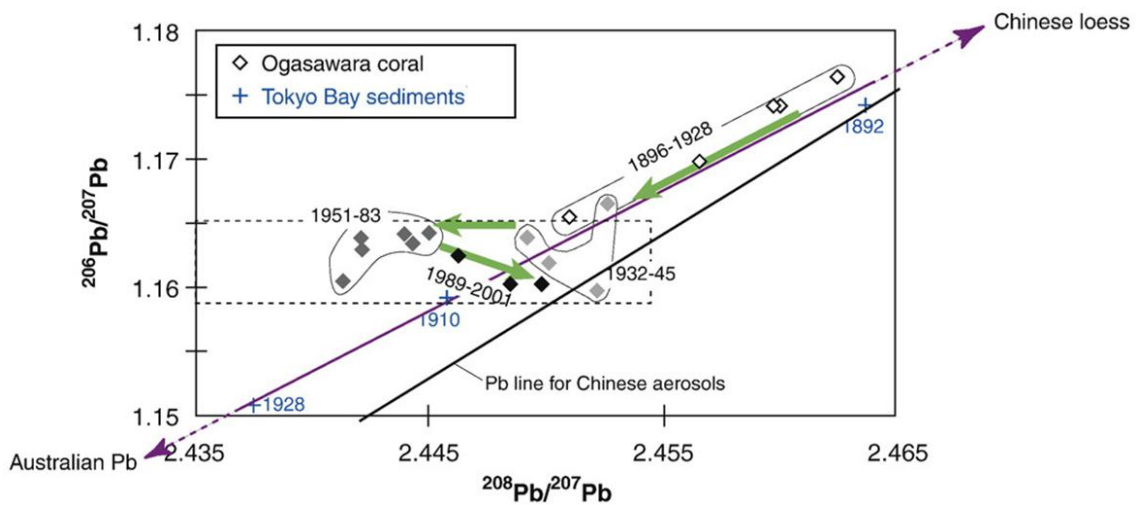
Figure 1.6 Temporal variation of coral-inferred sea surface Pb isotopic records in Ogasawara, Japan (Inoue and Tanimizu, 2008).

Lead is one of the eight critical heavy metals, including arsenic, cadmium, chromium, copper, mercury, nickel, lead and zinc (Lado et al., 2008). It is a potent neurotoxin that can be accumulated in soft tissues and bone. Lead isotopes, widely used as environment "fingerprints", has been proposed to be robust tracers for anthropogenic pollution. For example, lead isotopic composition in coral skeleton was used to reconstruct local and regional sea surface pollution history over the past centuries (Shen and Boyle, 1987; Inoue and Tanimizu, 2008).

1.3   Pb isotopic analytical technique

Mass spectrometry, either with thermal ionization (TIMS) or inductively coupled plasma (ICP-MS) as the ion source, has been successfully applied to Pb isotopic studies (Komáreka et al., 2008). The ICP-MS instruments include those with quadrupole-based (ICP-QMS), sector-based (or sector field) (ICP-SFMS) and time-of-flight-based mass analyzers (ICP-TOF-MS). Furthermore, the sector-based techniques can be equipped with single (SC) or multiple collector (MC) detection.

Two normalization methods have been successfully used over the past decade. One method is isotope dilution techniques using different double- or triple-spike recipes (^{205}Pb-^{202}Pb, ^{207}Pb-^{204}Pb and ^{207}Pb-^{206}Pb-^{204}Pb, 2 or more enriched Pb isotopes) have been used on TIMS to monitor mass fractionation (Woodhead et al., 1995; Todt et al., 1996; Galer and Abouchami, 1998, Makishima et al., 2007). The other method is to use thallium internal standard (^{205}Tl/^{203}Tl) for Pb instrumental fractionation correction in ICP-MS instruments (Collerson et al., 2002; Thirlwall et al., 2002; Weiss et al., 2004; Lo, 2008).

1.4   Challenge and Purpose

Since massive corals dwelling in tropical to subtropical regions show clear annual bands, the coral skeleton has been considered as a promising tool for reconstructing annual-decadal trends of industrial history and environmental change over the past hundreds years (Shen and Boyle 1987; Reuer et al, 2003; Inoue and Tanimizu 2008).

However, application of coral skeletal Pb isotope ratios to climatic/environmental changes has been a challenge in past decades. Only multi-annually resolved coral skeleton Pb isotopic records could be established (e.g., Shen and Boyle 1987; Inoue and Tanimizu 2008). Despite ppm-level Pb in crustal rocks, the low Pb content of only 10s-100s ng/g has hindered measurements of monthly-resolved coral Pb isotopic records and limited its applications. The low coral Pb level is attributable to low Pb concentration of ~ 10s ppb (1 ppb = 10^{-9}) in open ocean supplying largely from the atmosphere in dissolved form with a short residence time of 1~10 year. As offshore corals, possible sources for dissolved Pb are mobilization during weathering and dissolution of oxihydroxide coatings with subsequent release from porewaters and riverine inputs (Hinrichs et al.,2002).

To explore new and frontier application of monthly-seasonal resolution Pb records to environmental/climatic studies, a living coral *Porites* head was

collected from Son Tra Island, central Vietnam, nearby the largest industry city, Da Nang of Vietnam. In this study, I improved chemistry, reduced overall procedural blank, established a protocol of Pb isotopic determination in nanogram-to-picogram quantities by MC-ICP-MS, and measured Pb isotopic ratios in the collected coral *Porites* from A.D. 1978 to A.D. 1982 as an example. Pb concentration and isotopic records in central Vietnam show seasonal-annual variations, which had never been reported before in literature.

Chapter 2 Experiment Procedure

2.1 Regional settings and sampling

Son Tra Island is a block of Paleozoic granite located at central Vietnam (Figure 2.1). The annual sea surface temperature of satellite average is 27.2 $^{\circ}$C and the 18-year (A.D. 1994-2011) annual mean precipitation is 2374.2 mm (Vietnam government annual report). In central Vietnam, the coastal lowland is usually dry and hot in summer, from May to August with air temperature of 28.3-29.5 $^{\circ}$C, as the Truong Son Mountains obstruct moisture source from southwestern monsoon from April to October. The rainfall season concentrates from September to December by northeastern monsoon and occasional typhoon rain ranges from July to November.

A living massive *Porites* coral, 30 cm in length and 30 cm in diameter, was collected at a water depth of 4 m by Son Tra Island, 1 km offshore central Vietnam (16°12'59.4"N, 108°11'57.1"E) on June 14, 2005 (Figure 2.2). According to the annual bandings, the growth rate is 9.6-12.8 mm per year. A hiatus occurs at a depth of 14.7 cm from top. High-precision ^{230}Th dating and Sr/Ca record constrain the occurrence of this discontinuity between the summer and fall of 1991 for 2-3 months (Shen et al., 2012). Filtered water samples were collected from Han River, Cu De River and Da Nang Bay on February

19th and June 1st of 2009. Water samples were acidified with 0.2-ml 14 N

HNO_3 in the field to avoid possible growth of bacteria and plankton.
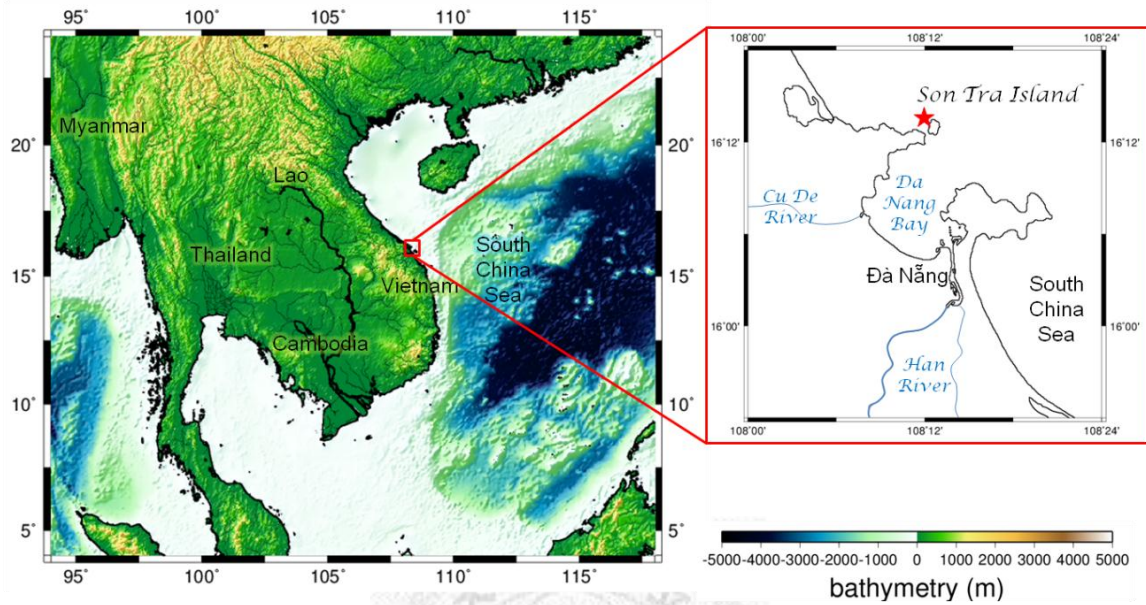
Figure 2.1 Topography of west South China Sea region. A living 30-cm *Porites* coral head was collected from Son Tra Island (red star symbol in the enlarged map), central Vietnam.
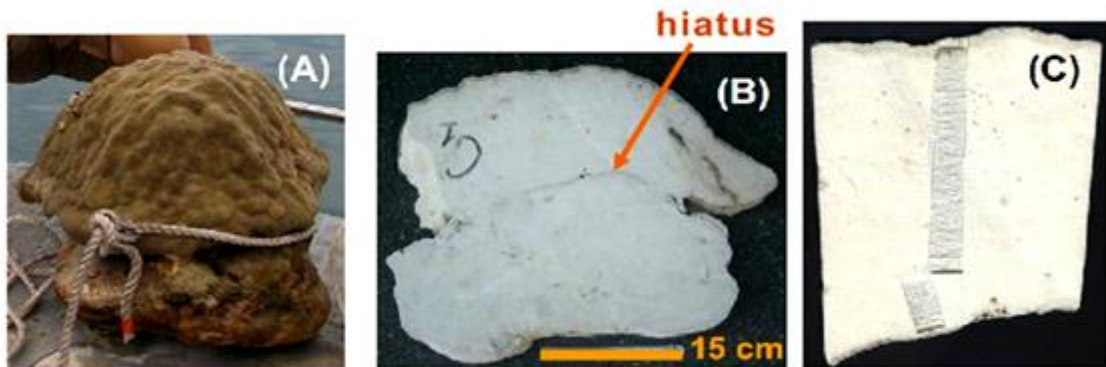
Figure 2.2 (A) Photo of the 30-cm modern *Porites* coral head used in this study. (B) The sliced coral slab, 0.5 cm in thickness; (C) A coral slab with sawed subsamples, 0.7 mm in width, corresponding to 0.7-1 month (modified from Chang, 2007).

2.2 Labwares

Chemistry was performed on a class-100 bench in a class-10,000 HISPEC clean room. Teflon labware, including 250-ml squeezing bottles, 30-ml dripping bottles, 7-ml Savillex beakers, 2-ml vials, and in-house heat-shrink columns (Figure 2.3), were acid-cleaned to reduce chemistry blank. The cleaning steps are as follows:

(i)   Rinse three times with Milli-Q ultrapure water.

(ii) Boil on hot plate in 50% aqua regia (J.T. Baker RG grade) for 4-5 hours.

(iii) Rinse three times with Milli-Q ultrapure water and boil in diluted redistilled HCl (J.T. Baker RD grade) for 4-5 hours.

(iv) Rinse three times with Milli-Q ultrapure water.

(v)   Fill containers with 1% aqua regia + HF (J.T. Baker ultrapure grade) for at least 10 days.

(vi) Heat on hot plate with a temperature set at 150 ^{o}C for 1.5-2 hours before rinse each item three times with Milli-Q ultrapure water and dry it on a class-100 bench.

In-house porous PE frits used to hold resin in Teflon column were cleaned as follows: Frits were kept in 10% H_2O_2 solution for 12 hours to decompose adsorbed organic matters, followed by rinse with ultrapure water couple times. Frits were cleaned successively with warm 1:10 aqua regia (J.T. Baker RG

grade) and diluted HCl (J.T. Baker RD grade) for 4-5 hours, and then rinsed

with ultrapure water couple times. Frits were then kept in a 30-ml Teflon

beaker with 8 N HCl (J.T. Baker ultrapure grade) for days and then cleaned

with ultrapure water 3 times. The last step was repeated 2-3 times. Before

using the clean frits, they were kept in 8 N HCl for one night.
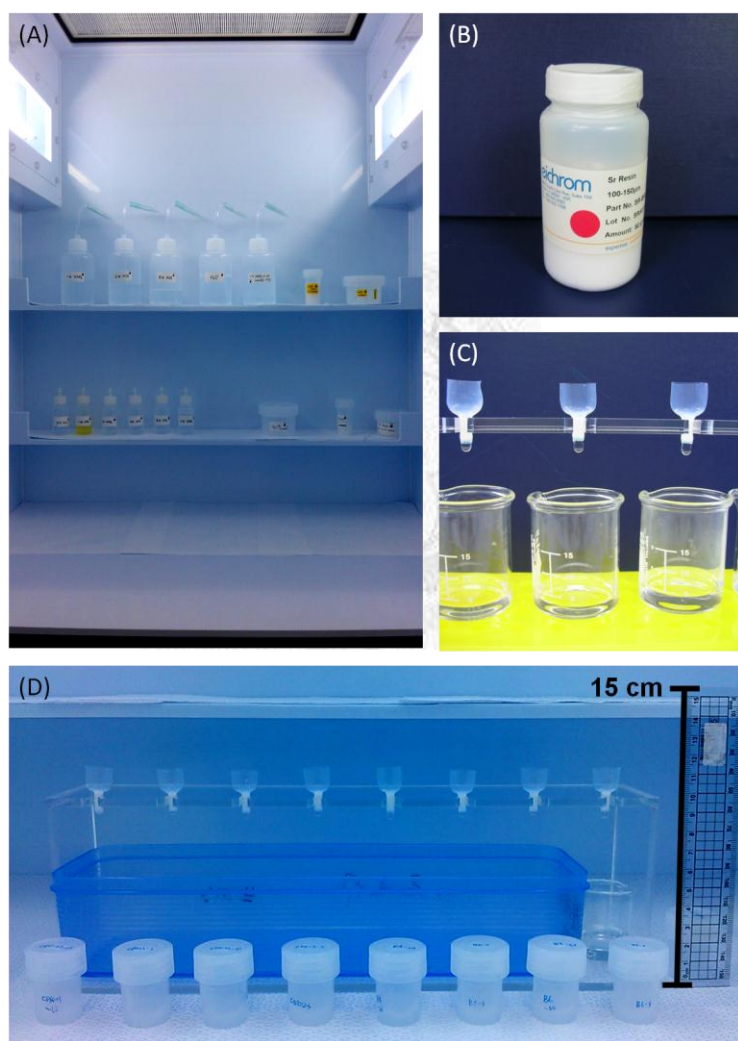
Figure 2.3 (A) A class-100 chemistry bench in a class-10,000 clean room; (B) Eichrom

100-150 mesh Sr-spec resin; (C) 9-mm in-house Teflon column; (D) 7-ml

Savillex beakers (front) and column holder with 8 Teflon columns (rear).

Eichrom 100-150-mesh Sr-spec resin, with a functional group of 4,4'(5')-di-t-butylcyclohexano 18-crown-6 (crown ether) in 1-octanol (Figure 2.4), was used for Pb purification from carbonate matrix. Before chemistry, 8-10 ml new resin was pre-cleaned successively with acids as following: (i) Milli-Q ultrapure water (40 ml x 3), (ii) 8 N HCl (RD grade, 40 ml x 3), (iii) Milli-Q ultrapure water (40 ml x 3), (iv) 2 N HNO3 (seastar, 40 ml x 4) , (v) Milli-Q ultrapure water (40 ml x 3), (vi) 8 N HCl (seastar, 40 ml x 4), and (vii) Milli-Q ultrapure water (40 ml x 3).
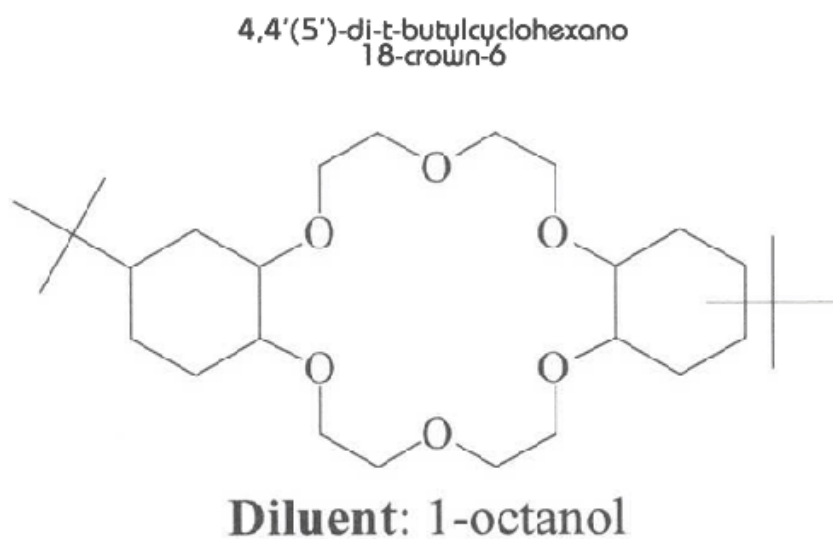
Figure 2.4 The molecular structure of Eichrom Sr-spec resin with an ether functional group.

2.3   Coral subsampling and pre-cleaning procedure

Procedure of subsampling monthly coral cubes and pre-cleaning is described below:

(i)   By microsurgical techniques, subsample was sawed every 0.7 mm, corresponding to 0.7-1 month, along the maximum growth axis on a 0.5-cm coral slab, cut from the collected coral head (Chang, 2007).

(ii)   Subsample, 5-10 mg, kept in acid-cleaned Teflon beaker, was cleaned with Milli-Q ultrapure water in an ultrasonic bath for 20 minutes.

(iii) Subsample was then cleaned with 10% H_2O_2 and 1 N NaOH at 50 ^{o}C for 1 hour to remove organic matter and rinse twice with Milli-Q ultrapure water.

(iv)   Subsample was polished with 0.005 N HNO_3 for 15 minutes and then washed twice with Milli-Q ultrapure water.

(v)   The cleaned subsample, approximately 1-8 mg, was dissolved in 1 N HNO_3, treated with 1 drop 10% H_2O_2, and then refluxed over 3 hours on hot plate set at 200 ^{o}C.

(vi)   Subsample solution was dried and re-dissolved in 0.09 ml 1 N HNO_3.

2.4   Chromatographic separation process

Chromatographic separation procedure was operated as follows (Figure 2.5). (i) Column was cleaned with 0.75 ml of 1 N HBr, and then 1 ml of 8 N HCl. (ii) The column was then pre-conditioned with 2 ml of 1 N HNO_3 after rinsing with 2 ml of Milli-Q ultrapure water. (iii) Sample solution in 1 N HNO_3 from Section 2.3 was loaded into column. Major elements, Mg, Ca, and Sr, and other trace metals were eluted by adding 0.75 ml of 1 N HNO_3 and then 0.75 ml of 2 N HCl. (iv) Pb fraction was collected with 1 ml of 8 N HCl in a 7-ml Teflon beaker. After chromatographic separation, the solution was dried, changed to nitrate form by adding 0.03 ml of 14 N H NO_3, and finally dissolved in 1 N HNO_3 + 0.025 N HF for instrumental analysis.
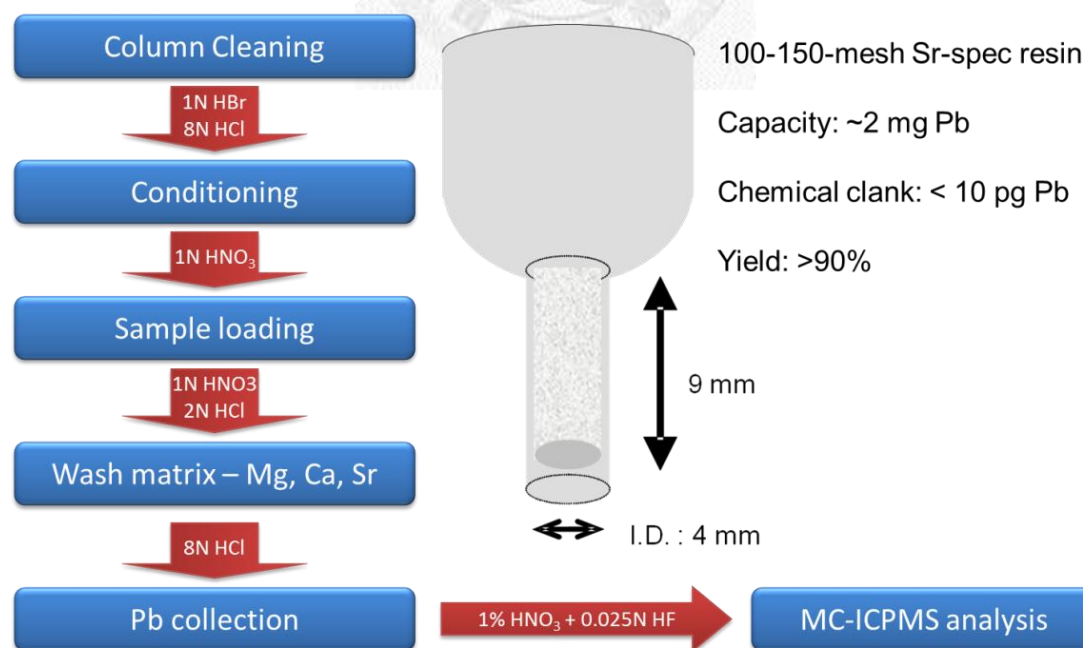
Figure 2.5 Flow chart of chromatographic separation (modified from Lo, 2008).

With this improved chromatographic separation method, Major elements, including Mg, Ca and Sr, could be effectively eluted with 1 N HNO_3 and 2 N HCl. Pb fraction was then collected using 8 N HCl (Figure 2.6). Chemical yield was better than 90% (Gale, 1996).
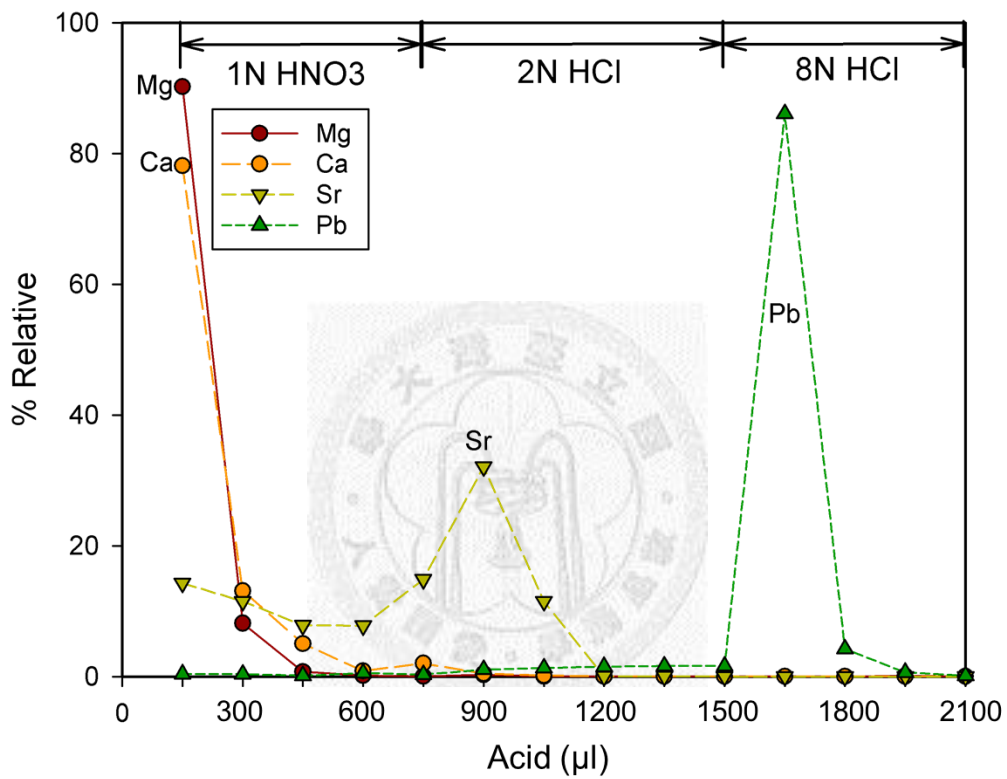
Figure 2.6 Chromatogram of separation of Pb from carbonate samples using Sr-spec resin. Major elements were separated with 0.75 ml of 1 N HNO_3, and 0.75 ml of 2 N HCl. The sequentially eluded Pb fraction with 8 N HCl was collected for MC-ICPMS analysis (modified by Lo, 2008).

2.5   Double-spike techniques for procedural blank

Overall procedural Pb blank is determined using ^{204}Pb-^{207}Pb diluted double spike solution (^{204}Pb-^{207}Pb) with 7.5 pg of 204Pb isotope. The ~ 1-ml double spike solution was added into 7-ml Teflon beakers, and treated with all chemical and instrumental procedures. Procedural blank was calculated from measured ion beam intensities of ^{204}Pb and ^{208}Pb of eluted solution on MC-ICP-MS with a single SEM protocol in electrostatic peak hopping mode.

Chapter 3 Instrumentation

3.1   MC-ICP-MS

Pb concentration and isotopic composition were measured on a MC-ICP-MS, Thermo Electron NEPTUNE, housed at the Department of Geosciences, National Taiwan University (Figure 3.1). The instrument is a double-focusing sector field mass spectrometer combining a magnet and an electronic field.

Figure 3.1 A MC-ICP-MS, Thermo Electron NEPTUNE, equipped with a class-100 PP hood on working bench.

3.2   Introduction system

A micro autosampler, Cetac ASX-100, and a desolvating nebulization device, Cetac Aridus, with a nebulizer (ESI-20) were used as sample introduction system (Figure. 3.2). The sample solution uptake rate was 40-60 µL/min. This system can dry sample mist to particulate, remove H_2O and acids, and to reduce element oxides and polyatomic interferences (Shen et al., 2002).
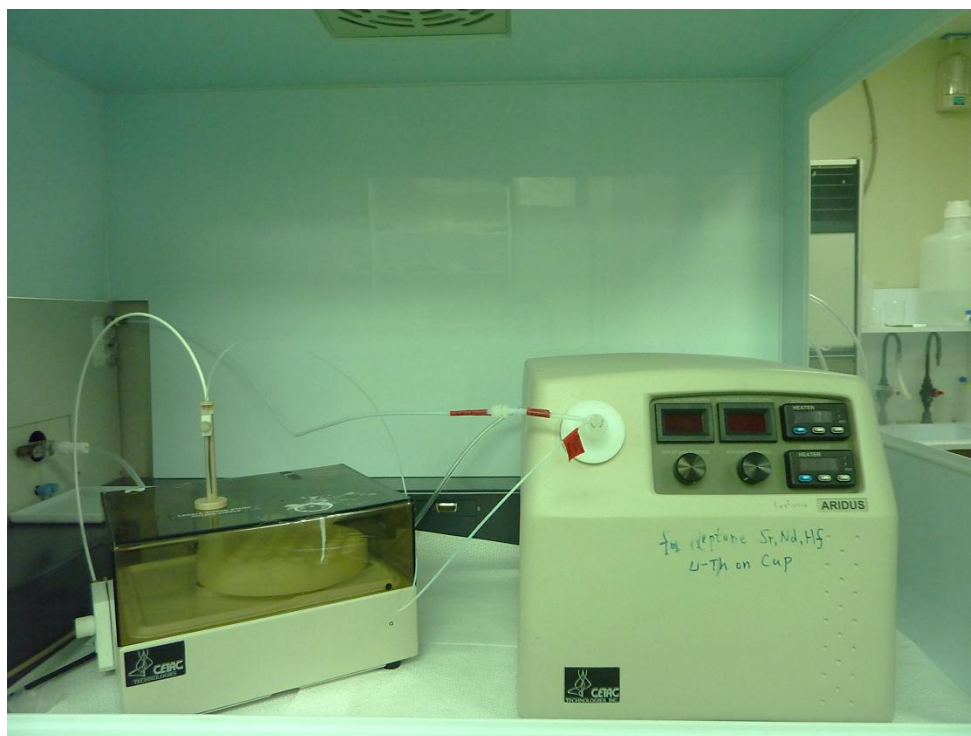
Figure 3.2 Sample introduction system with a micro autosampler, Cetac ASX-100 (left), and a desolvating nebulization device, Cetac Aridus (right), in a class-100 PP hood.

3.3   Instrumental setting and sensitivity

Settings of MC-ICP-MS are given in Table 3.1. Combined with a X-skimmer cone, jet sample cone, and updated interface pumping system, overall sensitivity (ion detected/atom introduced) was 3-5%. Typically, 1 ppb Pb standard solution with uptake rate of 50 µL/min gave 600 mV for ^{208}Pb.

Table 3.1   Instrumental settings

RF power (W)	1050 ~ 1200
Ar Cooling gas flow rate (L/min)	16.0
Ar Sample gas flow rate (L/min)	0.7 ~ 0.9
Ar Auxiliary flow rate(L/min)	0.9 ~ 1.15
Interface cones	Ni sampler and X-Skimmer
Fore vacuum (mbar)	2.31 E-4
High Vacuum (mbar)	1.0-1.3 E-7
Ion Getter (mbar)	0.9-1.0 E-8
Aridus spray chamber temperature (^{o}C)	110
Aridus desolvator temperature (^{o}C)	160
Resolution	Low resolution
Uptake rate (µL/min)	40 ~ 60
Pb concentration (ppb)	0.5 ~ 50
Solution consumption per run (mL)	0.3 ~ 0.5
Acquisition time (min.)	10 ~ 12

3.4 Corrections

A quantitative estimate of the true analytic intensity (I_t) from the measured intensity (I_m) requires several established corrections, including mass spectral backgrounds associated with the Faraday cup offsets (I_f) (or baseline drifting), the solvent blank (I_s), the instrumental blank (I_i), the procedural blank (I_p), isobaric interferences (I_{iso}), and tailing interferences from ambient ion beams (I_{tail}). This can be written as (Reuer et al., 2003):

$$I_t = I_m - I_f - I_s - I_i - I_p - I_{iso} - I_{tail}$$ …………………………………….. Eq.3.1

In this study, five corrections (I_f, I_s, I_i, I_{iso}, and I_{tail}) were applied (Lo, 2008). The Faraday cup offsets (I_f) and instrumental blank (I_i) were measured before running sample. The instrumental blank (I_i) could be reduced to less than 0.1% of the original sample beam with a washout time of 5 min. If the following sample has a high difference of 3% in isotopic ratio, the instrumental blank can cause a trivial bias of 30 ppm, only 10% of long-term analytical error of 200-300 ppm (2 S.D.). The Faraday cup baseline variability is 2-5 µV.

The gain variability is less than 2-5 µV. The solvent, 1 N HNO_3 + 0.025 N HF, ultrapure acids from J.T. Baker diluted with ultrapure water were used for instrument analysis, contributing Pb blank level less than 1 ppt (I_s).

Three possible isobaric interferences (I_{iso}), ^{204}Hg, WO and ReO, have been noticed. Through column separation, the intensities of ion beams of WO^+

and ReO$^+$ in sample solution are not mearable. ^{204}Hg, 6.85% abundance of Hg,

in plasma Ar and in the ICP interface has been reported as an important

isobaric interference on ^{204}Pb. Hg level is only minimal in the samples of

interest; but, an ion beam intensity of 4000-5000 cps of ^{202}Hg was observed in

the Ar carrier gas from Ar tank. In most cases, isobaric inference of ^{204}Hg is

about 1000 cps (= 0.016 mV). The tailing interferences from ambient ion

beams (I$_{tail}$), ^{203}Tl and ^{205}Tl can bias the determination of ion beam intensity Pb

isotope, especially for the lowest-abundance ^{204}Pb. Lo (2008) suggested a

mixing ratio of Tl/Pb between 0.1~1 (^{205}Tl/^{208}Pb = 0.15-1.2), or tailing

correction is needed for ^{206}Pb /^{204}Pb and ^{207}Pb /^{204}Pb ratios. For the other

high-abundance Pb isotopes, such as ^{206}Pb, ^{207}Pb and ^{208}Pb, their ion beam

intensities were usually higher than ^{205}Tl ion beams; the effect of Tl tailing can

be ignored. The procedural blank (I$_p$) caused by labwares, sampling, cleaning

reagents and chromatographic separation was as high as ~50 pg (Kelly et al.,

2009). To determine isotopic composition of ultra-low Pb content, the overall

procedural blank was reduced to only 2-3 pg using a ^{204}Pb-^{207}Pb double-spike

method.

Instrumental mass fractionation, also called mass bias, is a well-known

and ineligible phenomenon in ICP-MS systems resulting from space charge

repulsion and ion beam defocusing effects. Space charge effects in ICP-MS

generally result in preferential heavy ion transmission (Reuer et al., 2003). In this study, Pb isotope ratios were normalized to ^{205}Tl/^{203}Tl = 2.3889 with an exponential law (Eq. 3.2). The exponential law assumes that the logarithmic fractionation $\beta = \ln (r/R)$ is expressed as a function of the mass log-difference $\Delta(\ln M) = \ln(M_2/M_1)$. The mass fractionation coefficient for Tl (fTl) was calculated as:

$$f_{Tl} = \frac{\ln(R_{Tl}/r_{Tl})}{\ln(M_{205}/M_{203})}$$

……………………………………….... Eq. 3.2,

where R_{Tl} is the "true" ^{205}Tl/^{203}Tl ratio, r_{Tl} is the measured ratio, and M represents the atomic masses (^{203}Tl = 202.9723 and ^{205}Tl = 204.9745). The Tl mass correction factor fTl was used to correct the measured Pb isotope ratios (Eq.3.3):

$$R_{Pb} = r_{Pb} \left(\frac{M_1}{M_2}\right)^{f_{Tl}}$$

……………...………………………... Eq.3.3,

where R_{Pb} is the "corrected" Pb ratio, r_{Pb} is the measured ratio, M_1 and M_2 are the atomic masses of any 2 isotopes (^{204}Pb = 203.9730, ^{206}Pb = 205.9745, ^{207}Pb = 206.9759, and ^{208}Pb = 207.9767).

3.5   Analytical procedure

The purified Pb solution with an appropriate additive Tl was dried through the dry introduction system, atomized and ionized in plasma zone, and then accelerated with an accelerating potential of V = 8000 volts, and then deflected and dispersed based on m/z ratio by a magnetic sector. Ion beams were finally collected simultaneously with Faraday cups (Table 3.2). Secondary electron multiplier (SEM), a detector to count ion number, was used to measure instrumental blank (I_i) and the solvent blank (I_s).

The cup configuration was designed to simultaneously measured ion currents of ^{200}Hg, ^{202}Hg, ^{203}Tl, ^{204}Pb, ^{205}Tl, ^{206}Pb, ^{207}Pb and ^{208}Pb at static mode. ^{202}Hg and ^{200}Hg were used to correct for the isobaric interference of ^{204}Hg on ^{204}Pb. The measured $^{205}Tl/^{203}Tl$ was used for Pb mass bias correction. The cup configuration is shown in Table 3.2.

Table 3.2 Cup configuration used for the Pb isotope measurements.

Nominal mass	200	202	203	204	205	206	207	208
Measured element				^{204}Pb		^{206}Pb	^{207}Pb	^{208}Pb
Interference				^{204}Hg				
For correction	^{200}Hg	^{202}Hg	^{203}Tl		^{203}Tl			
Faraday cup used	L4	L3	L2	L1	C	H1	H2	H3
Amplifier (Ω)	10^{11}	10^{11}	10^{11}	10^{12}	10^{11}	10^{11}	10^{11}	10^{11}

Before running sample, 6-min Faraday cup baseline and instrumental blank (on SEM) were measured. Sample data acquisition included 180 cycles with an integration time of 2.097 s/cycle in only 1 block. It took 10-12 minutes per sample including uptake time, wash time, and also the time for measurements of cup baseline and instrumental blank. A routine auto-run sequence was also developed (Figure 3.3) as:

blank0, standard (981-1), blank1, sample1, blank2, sample2, blank3, sample3, …, blankn, standard (981-2).

For coral samples, the instrumental memory blank from the residuum of previous samples could be reduced to less than 0.1% with a washout time of 3 min. If the blank was high after a 3-min wash, an additional wash solution of 1% aqua regia + HF was introduced to remove off Pb residual in the introduction system between every 2 samples. An off-line data reduction processes to re-calculate Pb isotopic compositions.
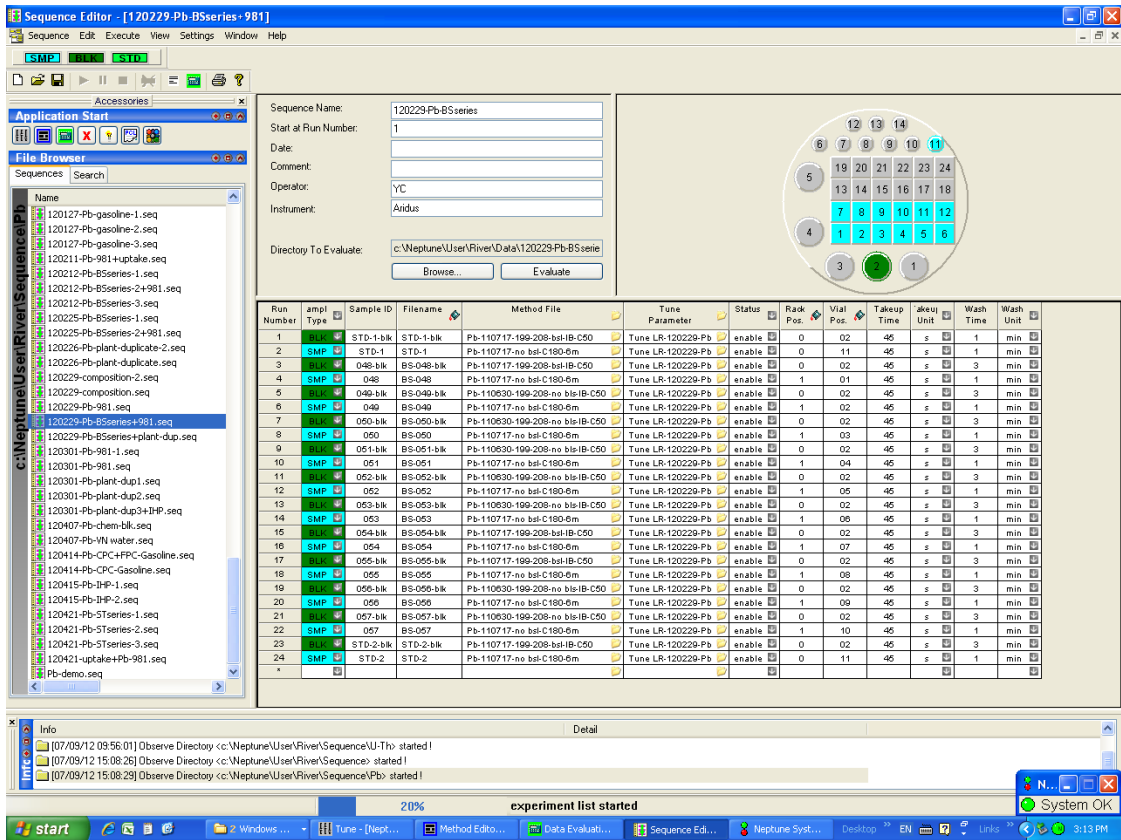
Figure 3.3 An auto-run sequence for Pb isotopic analysis on MC-ICP-MS.

Chapter 4 Results and Discussion

4.1   Procedural blank

I evaluated overall procedural Pb blanks for newly purchased Teflon

beakers and those used for 3-year carbonate U-Th dating. Surprisingly, Pb

blank in the fresh beakers, treated with 4-5 times of acid cleaning procedures,

is as high as 109 ± 63 pg. For the old Teflon beakers, Pb blank is only 2 ± 3 pg

(Figure. 4.1). Accordingly, I used old Teflon labwares in this study.
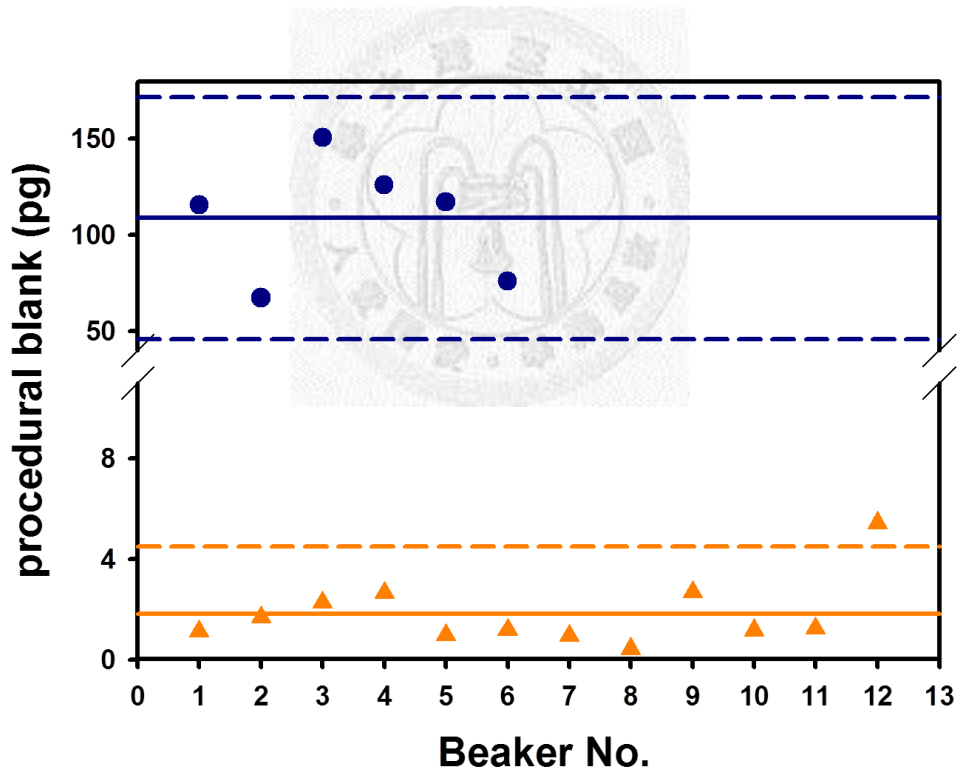
Figure 4.1 Procedural Pb blanks for acid-cleaned newly purchased Teflon beakers (blue)

and those used for 3 years (orange).

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4.2   Long-term reproducibility in picogram level

The long-term reproducibility of isotope ratios for different intensities with various sample sizes of 2-20 ng per measurement of NIST SRM 981, an international Pb standard, over a course of 12 months (2007/3-2008/4) were measured by Lo (2008) (Figure. 4.2(A)). The measured isotope ratios with 2-sigma external uncertainties are $^{206}Pb/^{204}Pb = 16.9411 \pm 0.0075$, $^{207}Pb/^{206}Pb = 0.91480 \pm 0.00012$ and $^{208}Pb/^{206}Pb = 2.1675 \pm 0.00035$. The measured Pb isotope ratios match the certified values within analytical error (Galer and Abouchami, 1998; Thirlwall, 2000; Thirlwall, 2002; Baker et al., 2004, Weiss et al., 2004).

To evaluate instrumental reproducibility for sample size less than 2 ng of Pb, we measured isotopic composition of NIST SRM 981 with small sample size of 250 pg (Figure. 4.2(B)). The measured isotope ratios with 2-sigma external uncertainties are $^{206}Pb/^{204}Pb = 16.949 \pm 0.036$, $^{207}Pb/^{206}Pb = 0.9145 \pm 0.0010$ and $^{208}Pb/^{206}Pb = 2.1671 \pm 0.0014$. Both internal and external uncertainties are better than 0.6‰ for isotopic ratios of ^{206}Pb, ^{207}Pb and ^{208}Pb. For the ratios with ^{204}Pb as the denominator, the 2-sigma external errors are up to 2‰, limited by Faraday cup baseline of 2-5 μV and small ^{204}Pb ion beam intensities of 4-25 mV.
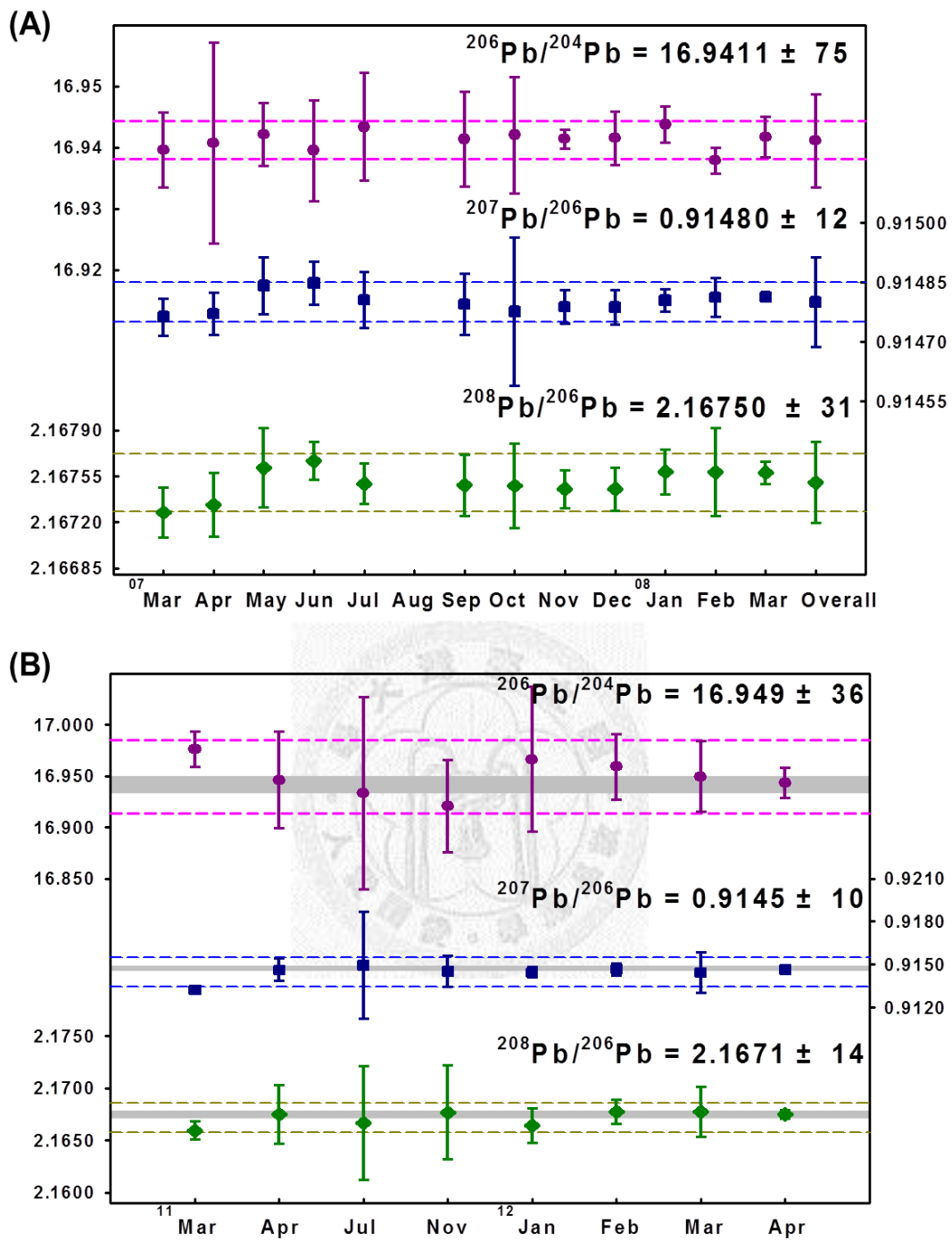
Figure 4.2 Long-term reproducibility of NIST SRM 981 with sizes of (A) 2-20 ng (Lo, 2008); (B) 250 pg (this study). The dotted lines present 2-sigma uncertainty external. Shadow zones in (B) represent the determined ratios for 2-20 ng of Pb from (A).

4.3   Blank and sample size

Most of high-precision Pb isotopic measurements requested 100s ng of Pb to overcome a chemistry blank of 100s-1000 pg and give high ion beam intensity during instrumental analysis (Weiss et al, 2004). Lo (2008) advanced measurement techniques. A small sample size of 10-20 ng of Pb was recommended to keep signal/blank ratio up of 1000 and good ion beam intensity for instrumental analysis. However, for monthly-resolved coral Pb isotopic analysis with a content of 10s-100s ng/g, the total amount of Pb in monthly coral subsample, 5-10 mg, is only 50s-1000s pg. The procedural Pb blank should be kept as low as possible. In this study, Pb procedural blank was improved to be reduced to only 2 ± 3 pg.

Replicate measurements made on standard NIST SRM 981 shows that our method can achieve a precision of $\pm$ 2‰ (2σ) with 300s-1000s pg of Pb (Figure. 4.3), equivalent to 5-10 mg of coral sample. When the sample is limited, the sample size can be as low as 300 pg. A sample size of 1.5 ng of Pb is recommended to offer external precision; the external precision is $\pm$ 400 ppm (2σ) for $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ and $\pm$ 900 ppm (2σ) for $^{206}Pb/^{204}Pb$.
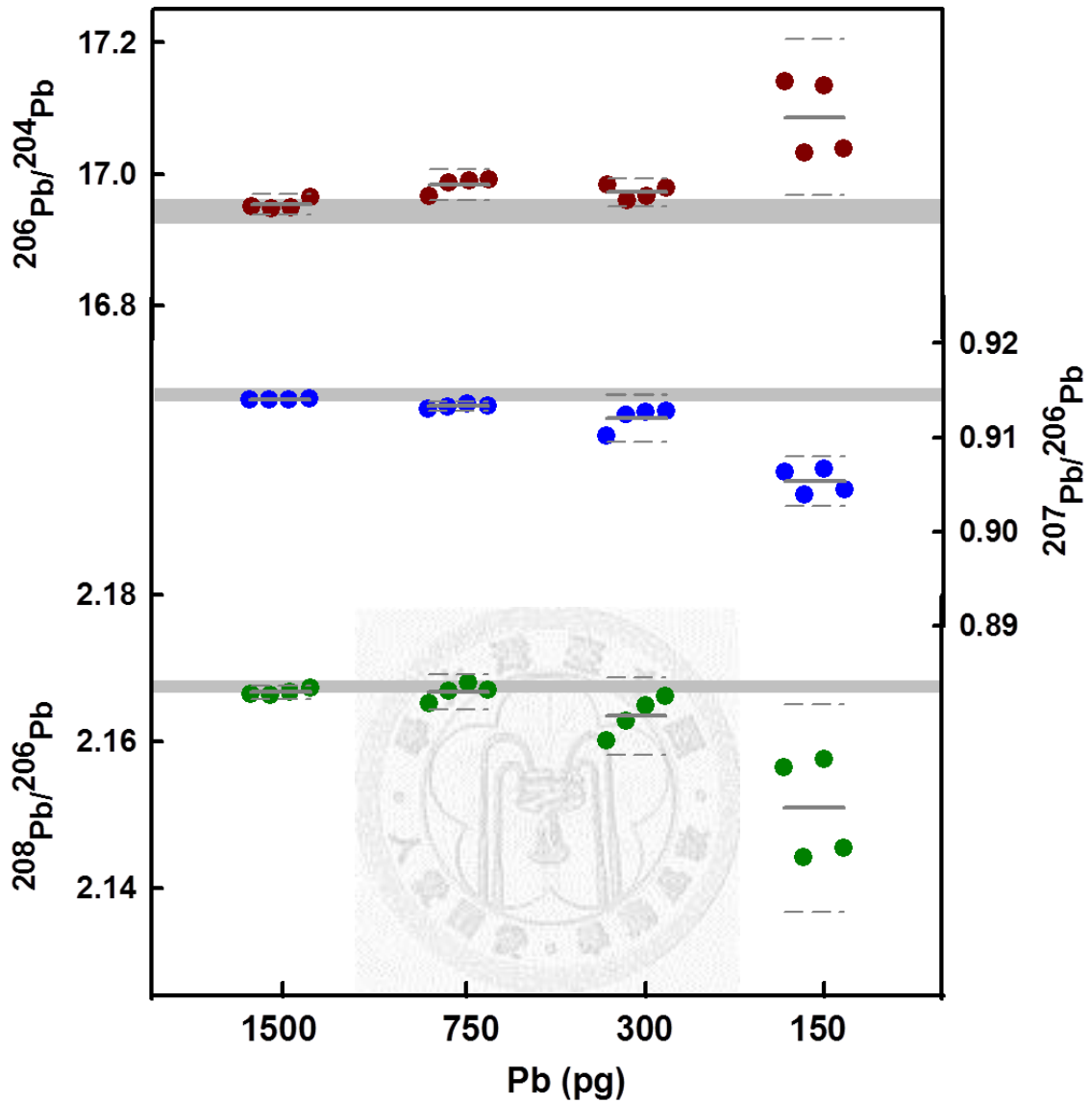
Figure 4.3 Reproducibility after chemistry processes in picogram-level of NIST SRM 981 Pb isotopic measurements. Solid lines denote the averages, dashed lines are 2-sigma ranges. Shadow zones represent long-term reproducibility with 2-20 ng of Pb. Accuracy is sound for sample size as low as 300 pg of Pb, but biased for 150 pg of Pb.

4.4   Duplicate analyses on coeval coral subsamples

To clarify our methodology and evaluate coral subsample representativity, we analyzed Pb isotopic compositions for four coeval monthly coral subsamples. Each subsample, 20 mg, contain 700 pg of Pb. The measured isotope ratios with 2-sigma external uncertainties are $^{206}Pb/^{204}Pb = 18.209 \pm 0.030$, $^{207}Pb/^{206}Pb = 0.8588 \pm 0.0011$ and $^{208}Pb/^{206}Pb = 2.1023 \pm 0.0012$. There is no significant difference of Pb isotope ratios between coeval subsamples. Two-sigma precision of 1‰ for all isotopic ratios can be achieved.
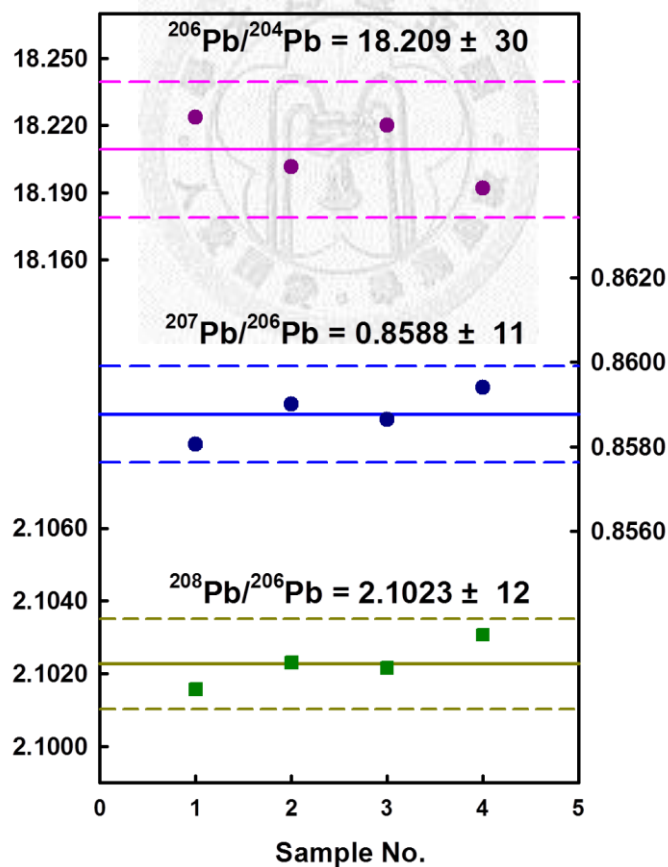
Figure 4.4 Replicate measurements of Pb isotope ratios for 4 coeval coral subsamples with 700 pg of Pb. Solid lines represent mean, and dashed lines $\pm 2\sigma$.

4.5   Pb concentration and isotopic records in A.D. 1978-1982

Monthly-resolution Pb isotopic records, 10-13 samples per year, during 1978-1982 are plotted in Figure. 4.5. Sea surface temperature (SST) data, inferred from coral Sr/Ca ratios (Chang, 2007), are used to calendar intra-annual coral subsamples. Pb isotopic ratios are 2.4262-2.4813 for $^{208}Pb/^{207}Pb$, and 1.1226-1.1745 for $^{206}Pb/^{207}Pb$. Features are exhibited as follows: First, monthly Pb isotopic data show clear seasonal-to-annual variations, which had never been reported before in literature. Second, in-phase relationships expressed for $^{208}Pb/^{207}Pb$ vs. $^{206}Pb/^{207}Pb$ time-series indicate end-member contributions between dry and wet seasons. Third, the Pb content time series shows an interannual gradual increasing trend.

Vietnam suffered in Vietnam War from 1959 to 1975. After the war, Vietnam economic began being developed. The trend of Pb concentration from 35 to 70 ppb during 1978-1982 may reflect the past reclamation condition of Da Nang, the current national biggest industry city, supported by a similar increasing trend of Ba/Ca data (Chang, 2007). When Da Nang began being developed, tremendous land use exacerbated flux of terrestrial sediment into the coastal zone. Interestingly, there are some high Pb-level peaks over 88 ppb (2σ) in summer and autumn during 1978-1982. Isotopic data are required to further clarify the possible sources.

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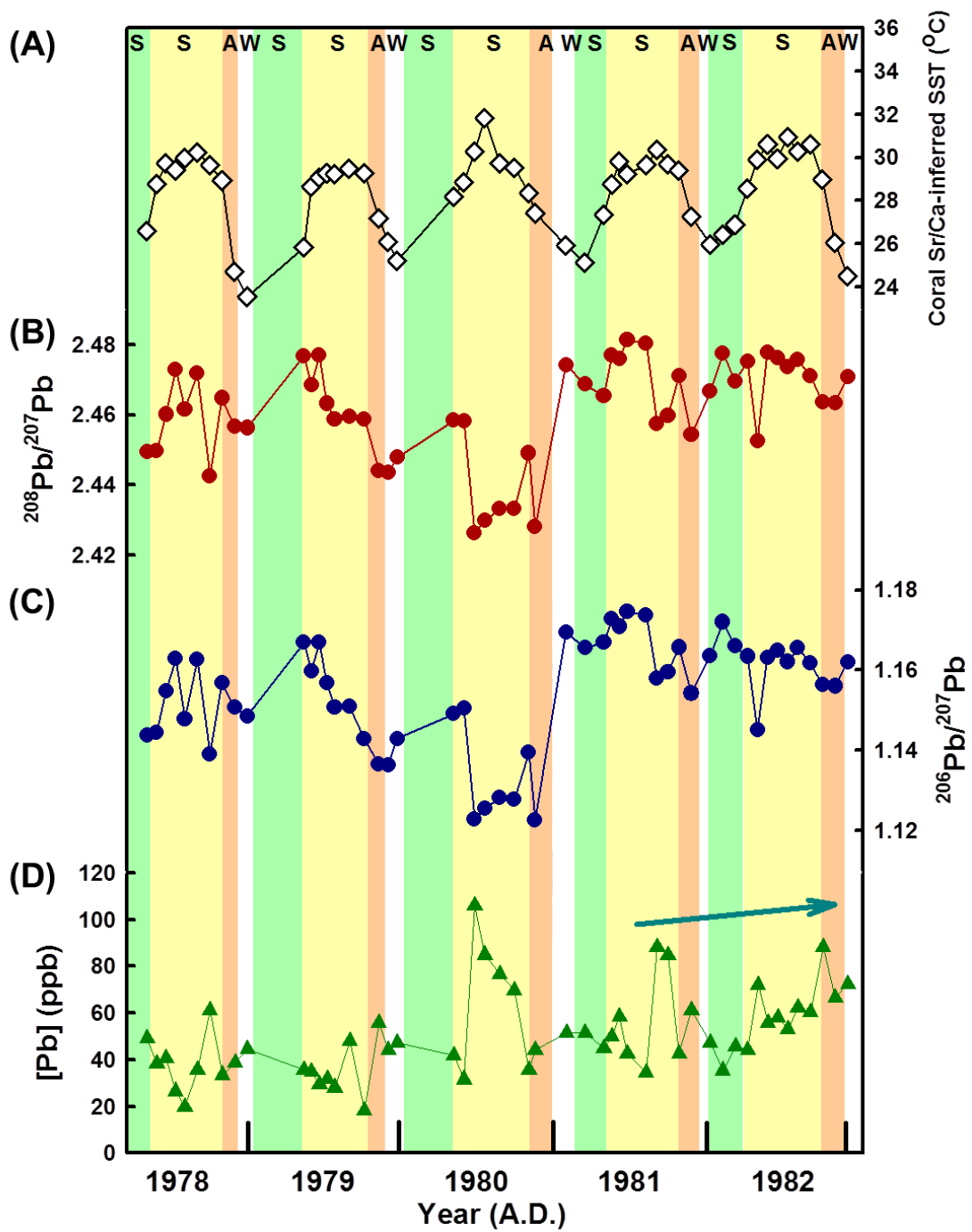**Figure 4.5** Monthly-resolved time series of coral (A) Sr/Ca-inffered SST, (B-C) Pb

isotopic ratios and (D) Pb concentration during 1978-1982. The arrow shows

a slow increasing trend of background Pb content since 1980. The error bars

are within symbol.

4.6   Possible Pb sources of central Vietnam

The natural dynamics of coral Pb isotopic data are associated with end-member contributions, including fluvial sediment, aerosol, airborne loess, and possible also adjacent open-ocean surface seawater. The isotopic compositions $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ show clear mixing between fluvial sediments ($^{208}Pb/^{207}Pb$ = 2.483-2.507; $^{206}Pb/^{207}Pb$ = 1.181-1.199) and adjacent open-ocean seawater from the South China Sea ($^{208}Pb/^{207}Pb$ = 2.445; $^{206}Pb/^{207}Pb$ = 1.147) (Figure. 4.6). Isotopic ratios are relatively high in dry season, may be attributable to airborne loess transported from mainland China.

Significant low $^{208}Pb/^{207}Pb$ (2.426-2.433) and $^{206}Pb/^{207}Pb$ (1.122-1.128) ratios are observed in summer and autumn of 1980 (Figure. 4.5). Combined with high Pb level, the isotopic data suggest an additional Pb source. The Pb isotopic characteristics of local Da Nang Bay water, riverine sediment, and South China Sea seawater are different from the isotopic data, indicating that they are not the candidates. In addition, Pb isotope composition of coral records in 1980 summer and autumn are different from that in aerosol samples from Ho Chi Minh, south Vietnam ($^{206}Pb/^{207}Pb$ = 1.155; $^{208}Pb/^{207}Pb$ = 2.430) , implying a possible long-distance Pb source. The coral Pb isotope ratios is close to those from Thailand ($^{206}Pb/^{207}Pb$ = 1.127; $^{208}Pb/^{207}Pb$ = 2.404), Malaysia ($^{206}Pb/^{207}Pb$ = 1.065-1.106; $^{208}Pb/^{207}Pb$ = 2.338-2.376) and Indonesia

$(^{206}\text{Pb}/^{207}\text{Pb} = 1.131; {}^{208}\text{Pb}/^{207}\text{Pb} = 2.395)$ (Bollhöfer and Rosman, 2001b).

Moreover, five day air-mass back trajectory clustering analyses (Figure. 4.7) show the transport ways which passing by Thailand, Malaysia and Indonesia, may support the Pb isotopic data. This similarity implies that the coral skeletal Pb content could be enriched by the aerosols, delivered by Asian summer monsoon and southwesterly flow after typhoon.
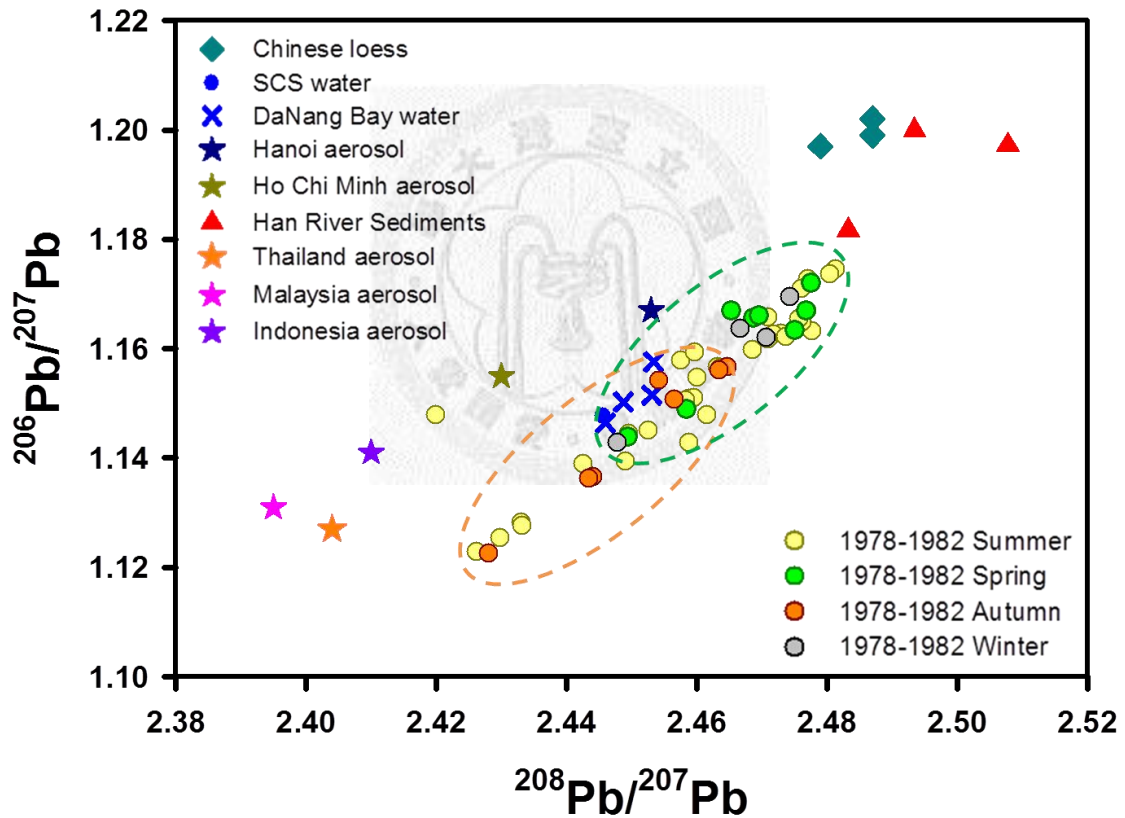
Figure 4.6 A plot of $^{208}\text{Pb}/^{207}\text{Pb}$ vs. $^{206}\text{Pb}/^{207}\text{Pb}$ for monthly coral *Porites* subsamples

(circles), Da Nang Bay water (cross symbols), Han River sediment

(triangles), Chinese loess (diamonds), and different regional aerosols (stars)

(Bollhöfer and Rosman, 2001b).
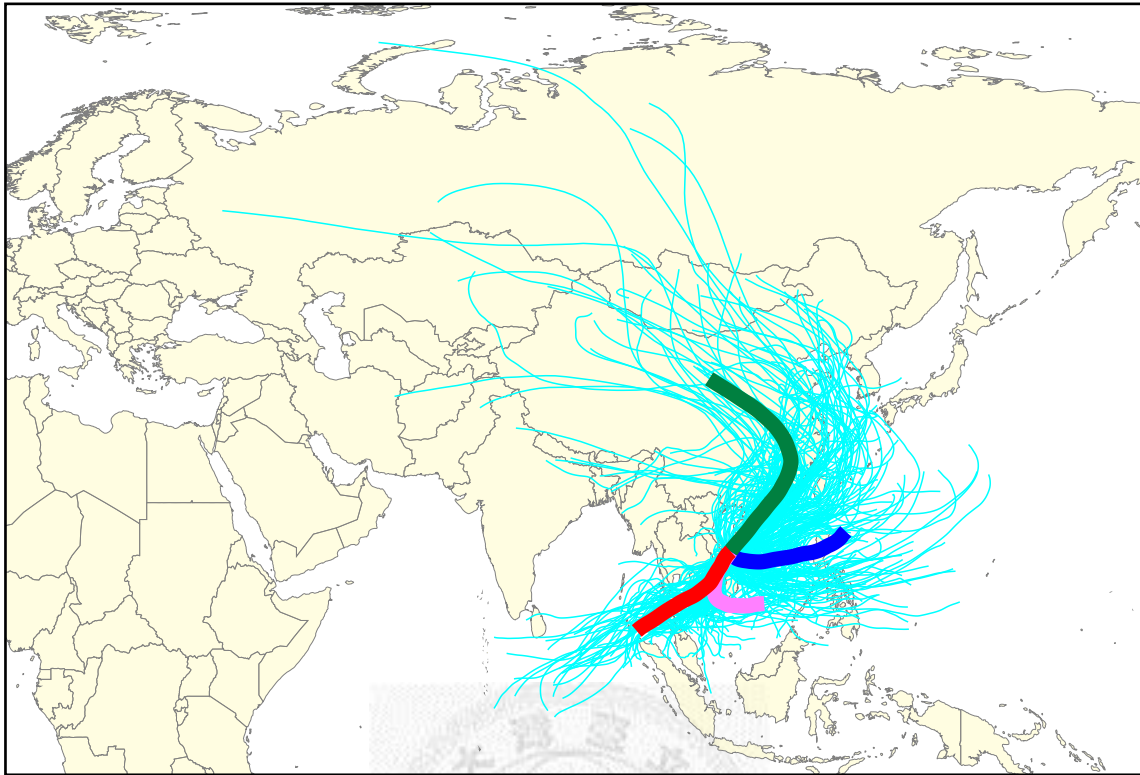
Figure 4.7 Five day air-mass back trajectory clustering analyses in the whole year 2010

using the NOAA HYSPLIY model, which were run once at 00:00 UTC each

day at an elevation of 500 m above sea level starting from 16.217^{o}N,

108.2^{o}E.

Chapter 5 Conclusions and Prospects

The key advantage of this study is to offer a possibility of analyzing Pb isotopic composition in pictogram quantities for natural samples, especially for those materials with limited Pb content. The first attempt here is to analyze monthly-resolution Pb data of a living coral *Porites* for reconstructing coastal seawater Pb isotopic history, distinguishing different sources pollutions. The results indicate that monthly resolved coral Pb isotopic sequence can be used as proxies and tracers for monthly-seasonal environmental changes and the impact of anthropogenic perturbation. This study indicates that coral Pb isotopic records can be potentially applied to better understanding of regional nature hydrological dynamics, planning of resource management, and making of sustainability policy.

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Appendix

Raw data of coral sample in A.D. 1978-1982 (* Mean ± 2 S.D.)

Sample ID	Year (A.D.)	$^{208}Pb/^{207}Pb$ *	$^{206}Pb/^{207}Pb$ *	Pb concentrations (ppb)	Sr/Ca	Sr/Ca-inferred SST (^{o}C)
BS-001	1978.333	2.4494 ± 0.0002	1.1438 ± 0.0001	49.2	9.034	26.607
BS-002	1978.396	2.4496 ± 0.0002	1.1444 ± 0.0001	38.2	8.896	28.769
BS-003	1978.458	2.4601 ± 0.0001	1.1547 ± 0.0001	40.8	8.835	29.724
BS-004	1978.521	2.4729 ± 0.0002	1.1628 ± 0.0001	26.6	8.854	29.420
BS-005	1978.583	2.4616 ± 0.0003	1.1478 ± 0.0002	19.9	8.819	29.965
BS-006	1978.667	2.4718 ± 0.0001	1.1626 ± 0.0001	35.6	8.803	30.225
BS-007	1978.750	2.4426 ± 0.0003	1.1390 ± 0.0001	61.1	8.839	29.662
BS-008	1978.833	2.4647 ± 0.0002	1.1567 ± 0.0001	33.5	8.886	28.917
BS-009	1978.917	2.4566 ± 0.0002	1.1507 ± 0.0001	38.6	9.154	24.713
BS-010	1979.000	2.4563 ± 0.0002	1.1485 ± 0.0001	44.5	9.228	23.564
BS-011	1979.375	2.4768 ± 0.0001	1.1669 ± 0.0001	35.7	9.082	25.845
BS-012	1979.427	2.4686 ± 0.0002	1.1598 ± 0.0001	35.0	8.902	28.663
BS-013	1979.479	2.4770 ± 0.0001	1.1669 ± 0.0001	29.6	8.876	29.081
BS-014	1979.531	2.4632 ± 0.0002	1.1567 ± 0.0001	31.9	8.863	29.289
BS-015	1979.583	2.4588 ± 0.0002	1.1508 ± 0.0001	28.1	8.866	29.228
BS-016	1979.681	2.4596 ± 0.0001	1.1510 ± 0.0001	48.1	8.849	29.496
BS-017	1979.778	2.4588 ± 0.0003	1.1428 ± 0.0002	18.1	8.863	29.283
BS-018	1979.875	2.4441 ± 0.0002	1.1365 ± 0.0001	55.8	8.998	27.164
BS-019	1979.938	2.4434 ± 0.0002	1.1363 ± 0.0001	44.3	9.065	26.110
BS-020	1980.000	2.4478 ± 0.0001	1.1428 ± 0.0001	47.3	9.122	25.215
BS-021	1980.375	2.4584 ± 0.0002	1.1490 ± 0.0001	41.9	8.933	28.178
BS-022	1980.444	2.4583 ± 0.0002	1.1505 ± 0.0001	31.6	8.890	28.866
BS-023	1980.514	2.4262 ± 0.0002	1.1228 ± 0.0001	106.0	8.801	30.259
BS-024	1980.583	2.4298 ± 0.0002	1.1254 ± 0.0001	85.0	8.701	31.828
BS-025	1980.681	2.4331 ± 0.0002	1.1282 ± 0.0001	76.5	8.834	29.736
BS-026	1980.778	2.4332 ± 0.0002	1.1277 ± 0.0001	69.6	8.849	29.504

Sample ID	Year (A.D.)	$^{208}Pb/^{207}Pb$ *	$^{206}Pb/^{207}Pb$ *	Pb concentrations (ppb)	Sr/Ca	Sr/Ca-inferred SST (^{o}C)
BS-027	1980.875	2.4490 ± 0.0002	1.1394 ± 0.0001	35.6	8.922	28.356
BS-028	1980.917	2.4280 ± 0.0002	1.1226 ± 0.0001	44.3	8.982	27.412
BS-031	1981.125	2.4743 ± 0.0001	1.1694 ± 0.0001	51.5	9.078	25.914
BS-032	1981.250	2.4687 ± 0.0001	1.1656 ± 0.0001	51.5	9.127	25.145
BS-033	1981.375	2.4653 ± 0.0001	1.1669 ± 0.0001	44.9	8.986	27.351
BS-034	1981.427	2.4771 ± 0.0001	1.1727 ± 0.0001	50.2	8.897	28.749
BS-035	1981.479	2.4761 ± 0.0001	1.1709 ± 0.0001	58.5	8.828	29.832
BS-036	1981.531	2.4813 ± 0.0001	1.1745 ± 0.0001	42.6	8.866	29.237
BS-038	1981.656	2.4804 ± 0.0001	1.1737 ± 0.0001	34.4	8.838	29.666
BS-039	1981.729	2.4575 ± 0.0002	1.1579 ± 0.0001	88.1	8.793	30.371
BS-040	1981.802	2.4597 ± 0.0002	1.1594 ± 0.0001	84.6	8.836	29.707
BS-041	1981.875	2.4710 ± 0.0001	1.1657 ± 0.0001	42.5	8.856	29.389
BS-043	1981.958	2.4542 ± 0.0003	1.1542 ± 0.0002	61.2	8.991	27.273
BS-045	1982.083	2.4667 ± 0.0003	1.1636 ± 0.0001	47.4	9.075	25.962
BS-046	1982.167	2.4776 ± 0.0002	1.1720 ± 0.0001	35.5	9.044	26.444
BS-047	1982.250	2.4696 ± 0.0002	1.1660 ± 0.0001	45.6	9.016	26.875
BS-048	1982.333	2.4751 ± 0.0001	1.1634 ± 0.0001	44.0	8.909	28.565
BS-049	1982.400	2.4526 ± 0.0001	1.1451 ± 0.0001	72.1	8.823	29.910
BS-050	1982.467	2.4777 ± 0.0001	1.1632 ± 0.0001	55.6	8.778	30.615
BS-051	1982.533	2.4762 ± 0.0002	1.1649 ± 0.0001	58.0	8.821	29.944
BS-052	1982.600	2.4737 ± 0.0002	1.1621 ± 0.0001	53.2	8.758	30.931
BS-053	1982.667	2.4757 ± 0.0002	1.1655 ± 0.0001	62.4	8.800	30.268
BS-054	1982.750	2.4710 ± 0.0001	1.1617 ± 0.0001	60.4	8.777	30.626
BS-055	1982.833	2.4636 ± 0.0002	1.1563 ± 0.0001	88.3	8.882	28.984
BS-056	1982.917	2.4634 ± 0.0002	1.1560 ± 0.0001	66.5	9.070	26.034
BS-057	1983.000	2.4707 ± 0.0002	1.1620 ± 0.0001	72.3	9.168	24.506