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Lead concentration and isotopic composition in the Pacific sclerosponge (*Acanthochaetetes wellsi*) reflects environmental lead pollution

Kazuto Ohmori[1]*, Tsuyoshi Watanabe[1]*, Masaharu Tanimizu[2]*, and Kotaro Shirai[3]*

[1]*Department of Natural History Sciences, Faculty of Science, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan*

[2]*Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 200 Monobe Otsu, Nankoku City, Kochi 783-8502, Japan*

[3]*Atmosphere and Ocean Research Institute, University of Tokyo, Kashiwanoha, Kashiwa-shi, Chiba 277-8564, Japan*

*E-mails: kazuto@mail.sci.hokudai.ac.jp ; nabe@mail.sci.hokudai.ac.jp; tanimizum@jamstec.go.jp; kshirai@aori.u-tokyo.ac.jp.

ABSTRACT

We measured Pb/Ca and Pb isotopes with high resolution in the high-Mg calcite skeleton of a Pacific sclerosponge (*Acanthochaetetes wellsi*) collected from the reef edge off the western coast of Kume Island (East China Sea), to investigate its potential to be used as a proxy for lead contamination in the environment, and atmospheric transportation and fallout over the last few decades. Skeletal Pb/Ca ranged from 58 to 1642 nmol/mol, 10 × higher than that of the aragonite skeleton of Pacific corals, and 2.5 × higher than that of the aragonite skeletons of Caribbean sclerosponges. The Pb/Ca timeseries recorded from 1967 through 2007 CE correspond to historical changes in atmospheric lead flux in anthropogenic aerosols.

Pb isotopes ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) in the sclerosponge skeleton document that the main source of lead emissions shifted from Japan (1970–1980 CE) to China (1995–2005 CE), as expected from the timing of legislation against the use of leaded gasoline in Japan and China. Our results indicate that the skeleton of the Pacific sclerosponge is a powerful proxy to monitor environmental lead pollution. Applying this methodology to long-living and/or fossil specimens could be useful in determining the interannual variability of atmospheric transport and dynamics over geologic time scales.

INTRODUCTION

Environmental lead (Pb) contamination is one of the most significant forms of heavy-metal pollution, which adversely affects blood pressure and the nervous system (Hilary, 2001). Throughout the 20th century, most Pb contamination in the environment was derived from anthropogenic aerosols, such as leaded gasoline, industrial emission and Pb ore dust (Chen et al., 2004). We must determine the long-term trends in anthropogenic Pb concentration order to gauge the influence of atmospheric Pb pollution.

The Pb content concentration and isotopic composition ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$) has been measured on samples from sediment cores (e.g.,Hirao et al., 1986), in order to identify temporal variations in atmospheric Pb contamination and the source of the Pb. The latter is possible because isotopic ratios differ between sites of origin. However, anthropogenic Pb aerosol particles have an atmospheric residence time of less than one week. Therefore these conventional geological proxies are difficult to use, because the rapid changes in Pb concentrations, and short fall-out events are not easily captured in cores accumulated at relatively low sedimentation rates. Alternatively, the lead content of coral skeletons has been analyzed to

reconstruct the history of lead pollution. Because coral skeletons grow quickly (0.5–2.5 cm/yr) and have distinct annual bands so that they can be dated precisely (e.g., Desenfant et al., 2006; Inoue and Tanimizu, 2008). However, the use of coral cores also presents difficulties: (1) the low lead concentration in skeletons (2–80 ppb) makes contamination control difficult and challenges the detection limits of analytical methods, and (2) the rapid growth rate of corals necessitates time–consuming handling.

We analyzed sclerosponges, which develop hard carbonate skeletons and may live for up to several centuries, at water depths ranging from 0 m to 300 m (e.g., Böhm et al., 1996). Their skeletal growth rates are usually very low (0.05–1.5 mm/yr) (Böhm et al., 1996; Fallon et al., 2003; Grottoli et al., 2010; Reitner and Gautret., 1996), but their skeletal Pb content is much higher than that in corals (0.1–2.3 ppm) (Rosenheim et al., 2005; Swart et al., 2002).

Geochemical analyses have shown that the Pb concentration in the aragonite skeletons of Caribbean sclerosponges (*Ceratoporella nicholsoni*) record the history of anthropogenic lead pollution since the industrial revolution (Lazareth et al., 2000; Rosenheim et al., 2005; and Swart et al., 2002). *Acanthochaetetes wellsi* is a long-lived sclerosponge species, occurring in the Indo-Pacific ocean, which secretes a high-Mg calcite skeleton. This species has been called a living fossil, because it has undergone very few morphological changes since its first appearance in the fossil record in the Lower Cretaceous (Reitner and Gautret., 1996). In this study, we analyzed the Pb/Ca ratios and Pb isotopic composition ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) of specimens collected at Kume Island, East China Sea, to investigate its potential as a proxy for environmental lead contamination and its atmospheric transportation and fallout.

MATERIALS AND METHODS

Materials

In March 2007, specimens of *A. wellsi* were collected from the reef edge (23 m depth) off the western coast of Kume Island in the East China Sea (26°21'N, 126°51'E) (Fig. 1). The anthropogenic Pb in these specimens is derived from eastern Asia, and has been carried northwards by the northwestern Asian winter monsoon (Wang et al., 2005). The skeletons were cut along their major axis of growth into 5-mm-thick slabs using a 0.2 mm diamond saw. The slabs were cleaned with deionized water, and dried for X-ray imaging. (Fig. 2) The distances between skeletal density bands were measured using the software program ImageJ (rsbweb.nih.gov/ij/).

Pb/Ca by LA-ICP-MS

Pb/Ca was analyzed at high spatial resolution by inductively coupled plasma–mass spectrometry (ICP-MS; 7500CS model, Agilent) coupled with a 213 nm Nd-YAG (Nd-doped yttrium-aluminum-garnet) laser ablation system in International Coastal Research Center, Japan. A polished slab of a sclerosponge skeleton which showed the most clear density bands was created by polishing with Al_2O_3 powder (<5μm) and cleaned, using Milli-Q water in an ultrasonic bath (5 min × 3 times). The skeleton was analyzed along its "tabulae" structure from the growing edge to the base of the specimen. Its total length was 3.8 cm, and we analyzed 748 points, at a spatial resolution of 50 μm, with laser spots measuring 50 μm in diameter. This resolution corresponds to one analysis for every 1.15 mo of growth. The reproducibility of the standard Pb/Ca value is was 3.27% (2σ, n = 10).

Pb Isotopes by MC-ICP-MS

Lead isotopes were measured by multicollector ICP-MS (MC-ICP-MS; Neptune,,Thermofisher Scientific, Germany) in Kochi Core Center Japan. We used a

computer-controlled microdrill to sample powders of the sclerosponge (~50 mg). Each sample was milled along the major growth axis, at right angles to the annual bands (~800 μm long, a width of 5 mm). In this study, Pb isotopes were measured in 15 samples with a high Pb/Ca value throughout the skeleton. The powdered samples were dissolved in 1 M HBr, and pure Pb fractions were collected on an anion exchange resin (Bio-Rad AG 1-X8). The Pb fractions were collected with 1.0 mL H_2O after the elution of other elements, using 2.0 mL of a mixed acid composed of 0.25 M HBr and 0.5 M HNO_3. The 15ng Pb was consumed in one 5 min analysis on the MC-ICP-MS. We corrected for isobaric interference of ^{204}Hg on ^{204}Pb, and background signal intensities determined with 0.15 M HNO_3 were subtracted from the analytical signals. Repeatability of the Pb isotopic standard, which consisted of a 10 ppb Pb and 1 ppb Tl solution, was $^{206}Pb/^{204}Pb$, 0.13%; $^{207}Pb/^{204}Pb$, 0.16%; $^{208}Pb/^{204}Pb$, 0.17%; $^{206}Pb/^{207}Pb$, 0.03%; $^{208}Pb/^{207}Pb$, 0.03% (2σ, n = 15). All data were normalized based on the deviation of the reported Common Lead Standard Reference Material (NIST SRM 981) values. The details of this method have been described by Tanimizu and Ishikawa (2006; Fig. DR2).

RESULTS

Both the density bands and Mg/Ca values exhibited distinct cyclic variations (~800–850 μm/1 cycle for density bands, and ~830 μm/1 cycle for Mg/Ca). The thickness of these bands corresponds to the annual growth rates previously reported for this species, so they correspond to annual layers (e.g., Grottoli et al., 2010). The profiles of Pb/Ca and lead isotopes were converted to a time series, using the extent of these annual bands and seasonal changes in Mg/Ca (detailed age model in the Data Repository). The average Pb/Ca measured by LA-ICP-MS in the skeleton of *A. wellsi* was 413 nmol/mol (n = 748), with values ranging from 58 nmol/mol to 1642

nmol/mol (Fig. 3A). The Pb/Ca values in the skeleton ranged from 200 to 300 nmol/mol, for the time period from 1970 to 1985 CE. During 1985–1997, the Pb/Ca ratio increased to 1400 nmol/mol. After 1997, the Pb/Ca ratio showed a rapid decrease from 1400 nmol/mol to 450 nmol/mol.

The Pb isotopic results obtained by MC-ICP-MS in specimen skeletons averaged 1.162 for $^{206}Pb/^{207}Pb$, and 2.442 for $^{208}Pb/^{207}Pb$. (n = 15) (Fig. 3B) Over time, the $^{206}Pb/^{207}Pb$ values increased until 1987 from the beginning of our records, and then decreased between 1988 and 2007. The $^{208}Pb/^{207}Pb$ values increased until 2000 and then decreased from 2000 to 2007.

DISCUSSION

Pb/Ca Profile

The atmospheric Pb in the East China Sea area is transportated by the Asian monsoon, absorbed on the surface of aerosol particles. These then are deposited in the ocean by dry deposition and/or rain washout. The Pb on the aerosol surface is then dissolved, and taken up into organic tissues and biogenic particles. Most Pb discharged by rivers into the oceans is deposited in sediments through particle scavenging (Nozaki et al., 1990), so that most of the dissolved Pb in the oceans is derived from aerosols. Therefore, the skeletal Pb in biogenic carbonate records the evolution of atmosphere-derived, anthropogenic Pb (e.g., Desenfant et al., 2006).

The maximum Pb/Ca observed in the Pacific sclerosponge (*A. wellsi*) was more than 1500 nmol/mol, ~2.5 × higher than Pb/Ca in skeletons of Caribbean sclerosponges (Lazareth et al., 2000; Rosenheim et al., 2005; Swart et al., 2002), and more than 10 × higher than Pb/Ca in coral skeleton (Inoue and Tanimizu, 2008). Sclerosponges obtain nutrition only by filter feeding particulates, which absorb heavy-metal species, thus concentrating the lead in their skeletal structure (Willenz

and Hartman, 1989). This biological characteristic, i.e., concentration of Pb into their skeleton, leads to relatively high concentrations which makes analysis easier, thus enables us to reconstruct metal contamination. In addition, the high Pb content in sclerosponge skeletons makes it possible to measure high-resolution lead isotopes.

Pb/Ca values vary seasonally (Fig. 3), possibly reflecting atmospheric circulation and the direction of the Asian monsoon winds along the northern coasts of the East China Sea (Fig. 1). Peak Pb/Ca values were recorded in late 1990s, in agreement with those in the profiles of coral skeletons from Ogasawara Island (Inoue and Tanimizu, 2008), and in sediments in this area (Hao et al., 2008). In addition, the evolution of Pb/Ca from the early 1990s to the mid-2000s shows the same pattern as the lead content of aerosols in urban areas (Beijing and Shanghai, Tianjin) around the East China Sea (Wang et al., 2006). Hence, the high-resolution Pb/Ca values in the skeletons of the Pacific sclerosponge (*A. wellsi*) indicate seasonal to interannual variations in atmospheric lead transport and ambient Pb pollution.

Reconstruction of Lead Emission Sources Using Pb Isotopes

Pb used by humans in fuel additives and industrial processes possesses specific isotopic compositions ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$) reflecting its origin and source area (e.g., Bollhöfer and Rosman. 2001). Biological isotopic fractionation effects are usually negligible, because the difference in relative mass numbers is small. Therefore the isotopic ratios of each end member contributes to the lead isotopic composition of biogenic carbonate skeletons, thus making these values a useful index in determining the source of lead pollution (Desenfant et al., 2006; Inoue and Tanimizu, 2008; Swart et al., 2002).

Our data on the lead isotopic composition of the Pacific sclerosponge (*A. wellsi*) suggest that the source of lead emissions shifted from Japan to China, as

reflected in the combined aerosols from ore deposits, natural sources, coal and unleaded vehicular exhaust (Fig. 4). The lead contribution of anthropogenic aerosols in the East China Sea thus varied dynamically :

(1) In 1973, the lead isotope composition was close to that predicted for Japanese aerosols, as observed using Hawaiian soil (Monastra et al., 2004).

(2) In 1973 and 1987, the values of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ increased to 1.166 and 2.441, respectively. This rise in lead isotope composition is considered to be due to a change in dominance of Pb from natural sources in China, because the use of leaded gasoline in Japan was limited in 1971 and banned in 1986.

(3) From 1987 to 1995, Pb/Ca increased and the $^{206}Pb/^{207}Pb$ values dropped to 1.160. These changes in Pb isotopes and Pb/Ca indicate that the coal and leaded gasoline increased due to industrial development in China (Hao et al., 2008).

(4) From 1995 to 2000, the $^{208}Pb/^{207}Pb$ value increased to 2.447, with Pb/Ca peaking in about 1997. The Pb isotope values strongly suggest an effect of industrial aerosol in Shanghai (Zheng et al., 2004). The Pb/Ca values reflect the limitation of the use of leaded gasoline in China in the mid-1990s.

(5) After 2000, Pb/Ca varied but declined overall, and $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ values decreased to 1.156 and 2.437, respectively. Leaded gasoline in China was banned in 2000. However, unleaded gasoline contains less than 100 ppb of lead contents that is derived from crude oil and lead isotopes of vehicular exhaust using unleaded gasoline reflect their value (Hurst, 2002). Thus, this low Pb/Ca and isotopic decline occurred due to a marked increase in the number of automobiles in China.

We compared these results with those for Pb isotopes in coral skeletons (Inoue and Tanimizu, 2008), which showed a similar trend, i.e., rising $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$

between the 1970s and early 1980s, and declining $^{208}Pb/^{207}Pb$ from the late 1980s to the early 1990s.

However, we could also detect a decline in $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ after 2000, probably caused by the limits posed on the use of leaded gasoline in China. These isotopic changes after the 1990s correspond to the records of Chinese atmospheric aerosols (Cheng and Hu, 2010).

Our findings indicate that Pb/Ca and the lead isotope composition of Pb in the skeleton of *A. wellsi* can be used to reconstruct temporal changes in atmospheric lead concentrations and their emission sources. *A.wellsi* are widespread across the Pacific and Indian Oceans, and have persisted over geological time, from the Cretaceous to the present. The application of this proxy suggests that using long-lived and/or fossil specimens will allow us to investigate century-scale variations in lead concentrations, emission sources, and atmospheric dynamics over geological time.

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APPENDIX: AGE MODEL

Figure 2 shows a comparison of the soft X-ray image of *A. wellsi* skeleton to the Mg/Ca, using LA-ICP-MS. High values of the grayscale indicate high skeletal density or horizontal structure areas. Our specimen has 38 density bands. Both the grayscale and Mg/Ca ratio show cyclic changes. The grayscale shows 800–820 μm/1 cycle, and Mg/Ca ratio shows ~830 μm/1cycle. In comparison, the grayscale bands and Mg/Ca in the skeleton show that high values of in grayscale have high Mg/Ca, and the reverse. (See more discussion in supplemental information.)

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FIGURE CAPTIONS

Figure 1. Sample location in the East China Sea. The arrows indicate northwest Asian monsoon occurs in northern hemisphere winter, with north to northwest winds (Wang et al., 2005). Pacific sclerosponges (*A. wellsi*) were collected by a reef enclosure on the western coast of Kume Island at 23m depth. (26°21'N, 126°51'E)

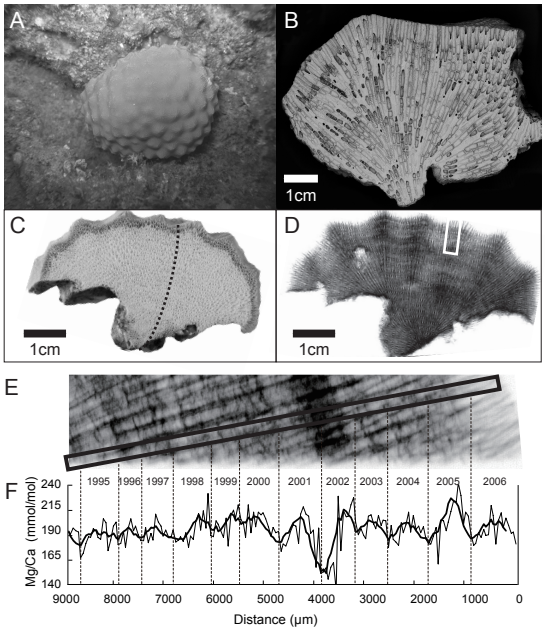
Figure 2. A: A Pacific sclerosponge (*A. wellsi*) from Kume Island, East China Sea. B: High-contrast image of skeletal cross section. These skeletons consist of tabulae structures. C: Photograph of a skeletal slab. Pb/Ca and Pb isotopes were analyzed along the dotted line, by laser ablation–inductively coupled plasma–mass spectrometry and multicollector–inductively coupled plasma–mass spectrometry. D: Positive soft X-ray image of skeletal slab (white rectangle shows area in E). Thickness of slab is 5 mm. E: Skeletal density bands in X-ray photograph. (surface to 9 mm depth). F: Mg/Ca in skeletal surface. Density bands reflect annual growth (Fallon et al., 2003). In general, Mg/Ca in biogenic aragonite records ambient environmental water temperature. Our model uses skeletal density bands and Mg/Ca variation (see the Appendix).

Figure 3. A: Time series of Pb/Ca in a Pacific sclerosponge (*A. wellsi*) skeleton, growing from 1967 through 2007. Dotted line shows LA–ICP-MS values; solid line represents 5-point mean values: $2\sigma = 0.14$ μmol/mol. B: Time series of $^{206}Pb/^{207}Pb$

ratio (filled circle, NIST SRM 981 mean) and $^{208}Pb/^{207}Pb$ ratio (open circle). All data were normalized based on the deviation of the reported NIST SRM 981 values. Ages were determined using Mg/Ca and density band counts.

Figure 4. Triple isotope cross plot of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios. A: Sources of Pb isotope ratios in *A. wellsi* skeleton (predicted Japanese aerosol in 1970–1980, Monastra et al. [2004]; Natural sources in China, Lee et al. [2007]; Pb ores in China, Hou and Zhao [1993]; coals in China, Bollhöfer and Rosman [2001]; industrial aerosols in Shanhai, Zheng et al. [2004]; vehicle exhaust, Chen et al. [2005]; Chinese Pb line, Mukai et al. [2001]). B: Temporal variation of Pb isotope ratios in *A. wellsi* skeleton.

[1]GSA Data Repository item 2014xxx, Age model, flow chart of preparation for Pb isotope measurements and comparison of Pb isotopes of sclerosponge and coral skeletons in the western Pacific Ocean during 1967–2007, is available online at www.geosociety.org/pubs/ft2014.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.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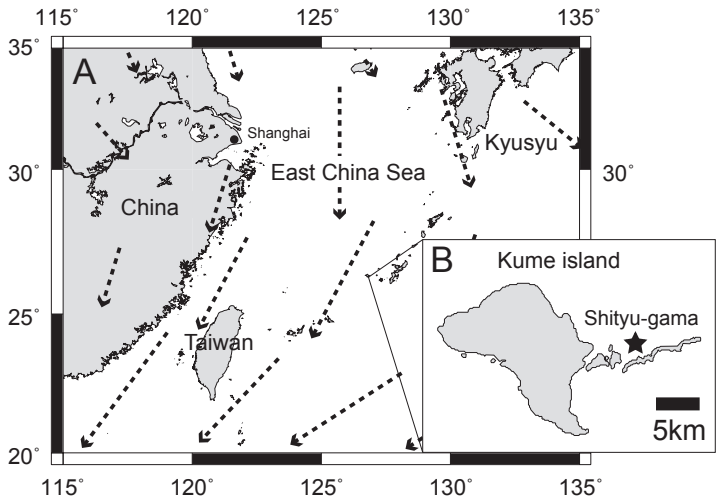

Fig. 1. Map of sample location. On East China Sea, the northwest Asian monsoon blow in winter. Pacific sclerosponge (Acanthocheatetes wellsi) was collected by a reef enclosure on the western coast of Kume island at 23m depth. Dot-arrows show direction of Asian winter monsoon that blow north to northwest over sample site. (Wang et al., 2005)

368

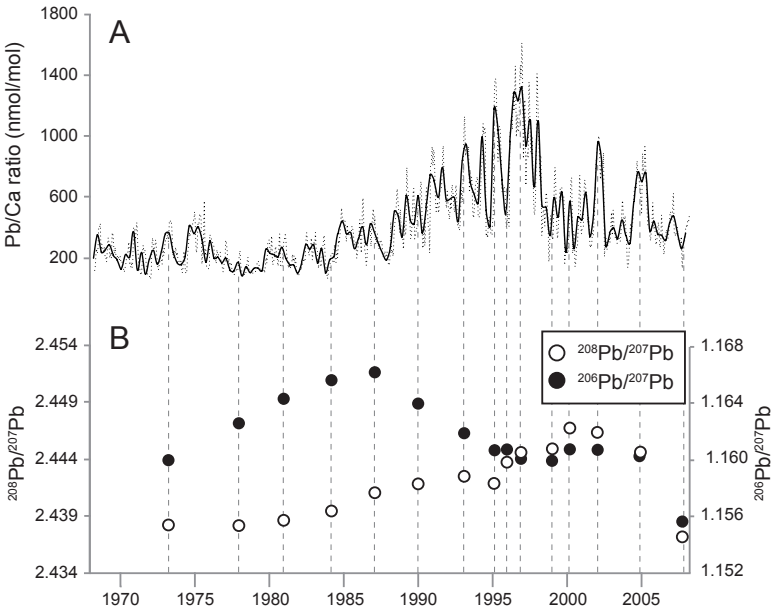

Fig. 3. Time series of Pb/Ca (A. dott line:LA-ICP-MS values, solid line:5 point mean values) ratios, ^{206}Pb/^{207}Pb (B. filled circle) and ^{208}Pb/^{207}Pb (B. open circle) records in pasific sclerosponge (Acanthocheatetes wellsi) skeleton during 1967~2007. Ages were determined by results of Mg/Ca ratios and counting the density bands.

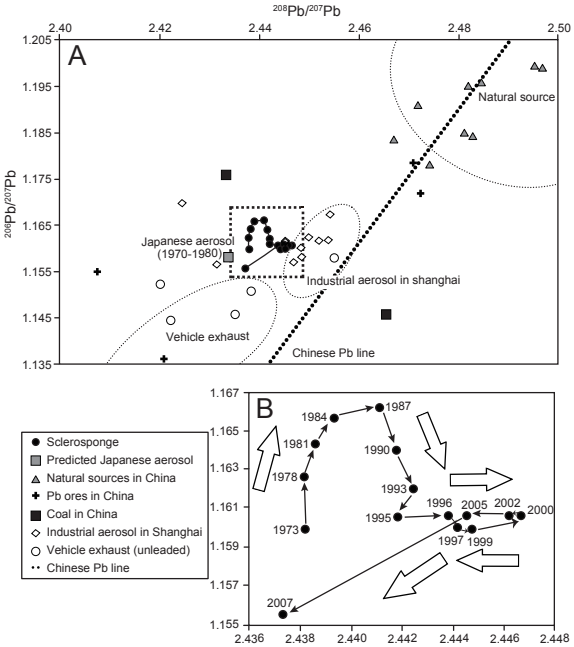

Fig. 4. Cros prot of $^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$ ratios. A) Sources of Pb isotope ratios in Acanthocheatetes wellsi skeleton (Predicted Japanese aerosol in 1970~1980; Monastra et al., 2004, Natural sources in China; Lee et al., 2007, Pb ores in China; Mukai et al., 1993 and Hou and Zhau.,1993, Coals in China; Bollhöfer and Rosman, 2001, Industrial aerosol in Shanhai; Zheng et al.,2004, Vehicle exhuast; Chen et al., 2005, Chinese Pb line: Mukai et al.,2001). B) Temporal variation of Pb isotope ratios in Acanthocheatetes wellsi skeleton.

370