Pb isotopes as the finger print for distinguishing between natural and anthropogenic sources

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Abstract

Pb isotopes can be used in the many ways to use their ratio isotopes for detecting natural and anthropogenic sources. We used the accuracy and precision of analytical methods using ICP-MS/TIMS and then normalized using the specific values of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$. The data references of ore Pb from Daylight-Errington toronto #359 mines as group-1 with age in 1900-3200 M.a to Manitauwadge Wilray #332-Snake Lake # 660* mines as group-4 with age in the present day were measured, calculated, and modified of lead isotope ratios using the single-stage model of stable isotopes from parent rocks. The lead isotope ratios as $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ were involved to convert $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ using $^{235}U/^{204}Pb$, $^{232}Th/^{204}Pb$ (present-day values), $^{238}U/^{235}U$ (present) with the time of decay constants $0.155125 \times 10^{-9}\ yr^{-1}$, $0.155125 \times 10^{-9}\ yr^{-1}$ and $0.155125 \times 10^{-9}\ yr^{-1}$. The new decay constants and the corrected ratios were found after choosing the assumsion time from present day to the classial age for production of lead growth curved. The values Pb isotope ratios of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ then were applied to lead growth curved for investigating and detecting the anthropogenic and natural inputs.

Keywords: Sediment, Pb isotopes, Anthropogenic, Natural Sources, Ore Pb

1. Introduction

Lead is devided the four main its isotopes and abundance such as ^{208}Pb (52%), ^{206}Pb (24%), ^{207}Pb (23%) and ^{204}Pb (1%). That Pb isotopes were released by the series decay chain products from primordial ^{238}U, ^{235}U, and ^{232}Th (except for ^{204}Pb). Three Pb isotopes, ^{208}Pb, ^{206}Pb, ^{207}Pb were radiogenically made in as the daughter products. The ^{204}Pb is used as the baseline to estimate excess radiogenic of Pb present in media samples. The excess of radiogenic ^{208}Pb, ^{206}Pb, ^{207}Pb can be measured as $^{208}Pb/^{206}Pb$ or $^{207}Pb/^{206}Pb$ to understand for adding the new Pb anthropogenic [1].

Besides of radiogenically Pb isotopes, the radioactive isotopes ^{210}Pb, ^{212}Pb, and ^{214}Pb were also determined to detect the history of lead inputs in the environment. Especially for ^{210}Pb, some researchers confirmed to calculate the dating of ice, sediment, pond sediment, and

peat deposits for history of pollution from ancient to modern time [2,3]. However, the analysis of Pb radioactives of the various exposure categories make analysis difficult for accuracy and precision.

In case of radiogenically Pb or Pb stable isotopes, from the process total Pb concentrations to ^{206}Pb, ^{207}Pb, ^{208}Pb and ^{204}Pb isotopes are not effected by the chemical fractionation processes. Pb isotope ratios then were chosen as a methode of accuracy and precision to determine the sources and their pathways of Pb pollution [4]. The Pb isotope ratios are commonly used as $^{206}Pb/^{204}Pb$, $^{208}Pb/^{206}Pb$ with $^{206}Pb/^{207}Pb$ or $^{207}Pb/^{206}Pb$ to invetigate the source of Pb [4–6]. In order to determine accuracy and precision of Pb isotope ratios, their normalization should have the lowest variability between errors. The abundance of ^{207}Pb has slightly changed with time compared to ^{206}Pb due to the effect of completely decayed by ^{235}U, while ^{238}U is more abundantly in the earth. In addition, the researcher did not use the ^{204}Pb for ratio isotope because of its stable abundant value and distinguish between Pb ratio isotope values.

$^{208}Pb/^{206}Pb$ with $^{207}Pb/^{206}Pb$ are used as track to the origin of Pb contamination in several media such as plants, mammals, river and ocean water, sediment, road-side dust [4–7]. The plot of their values of Pb isotope ratios in the growth curved of Pb is more important to distinguish the anthropogenic and natural of Pb. In the growth curved of Pb, some values of Pb isotope ratios undergo overlapping and indicates the sources of sample. Some researchers using the growth curved investigated sources of Pb [6,8] . In this study, we clearly reported how to use the lead growth curved of Pb and its assessment for $^{208}Pb/^{206}Pb$ with $^{207}Pb/^{206}Pb$.

2. Methodology

2.1 Calculation and Formation of Pb Growth Curved

In order to build the equations of building Pb growth curve, we used some references of the mines in the world. The measured of Pb isotope values were combinated in the radioanalytical chemistry equation using single stage 1 modelling [8]. The recent and oldest of mines correlated with the ages reflected the change of Pb isotope ratios. All of originally mines in the world measured by isotope ratios of $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$ were converted to $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ (Table 1). As list in Table 1, we have the references with our modified calculations start from recently mine to old sediment. We classified the 4 groups of mines based on the range of the geological age to understand the change of Pb isotope ratios [6,8]. Group-1 used the reference of Daylight to Errington mine toronto 359 indicating the lowest Pb isotope ratios of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ and the highest of their Pb isotope ratios of group-4 from Manitauwadge Willroy # 332 to Snake Lake # 660*. The pattern of value of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ of group-1 to group-4 undergoes the opposite in their values of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$.

Table 1 Pb isotope ratios of mines in the world

Samples	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	Geological Age (Ma)	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$
Group-1						
Daylight-Errington toronto # 359	12.4310-15.4890	14.0650-15.3030	32.2700-35.3380	1900-3200	2.5959-2.2815	1.1314-0.9980
Group-2						
Southwest - Finland-Balmat	15.6760-16.9350	15.3280-15.5050	35.2330-36.4230	1080~1700	2.2476-2.1508	0.9778-0.9156
Group-3						
Captains Flat -	18.0650 -	15.6140 -	38.1570 -	0 – 425	2.1122	0.8643
White island	18.7720	15.5980	38.6620		2.0596	0.8309
Group-4						
Manitauwadge Willroy # 332	13.2860	14.4110	33.1190	-	2.4928	1.0847
Snake Lake # 660	15.7090	15.2560	35.1760	-	2.2392	0.9712

- Geological age of present day

After modified the values of $^{208}Pb/^{206}Pb$ vs $^{207}Pb/^{206}Pb$, we need the assumption of time for production of Pb growth curved. The calculated of Pb isotope ratios from $1x10^9$ years to $4x10^9$ years are listed in Table 2.

Table 2 The assumption time using the single-stage model

t (x 10^9 year)	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
0	18.465	15.642	38.507	0.847	2.085
1	16.9284	15.531	36.678	0.917	2.167
2	15.134	15.232	34.757	1.006	2.297
3	13.0384	14.434	32.738	1.107	2.511
4	10.5913	12.296	30.616	1.161	2.891

We then Used the single-stage model of Russell and Reynolds with the formula as follows [8]:

$^{206}Pb/^{204}Pb = X = a + \alpha V(1-e^{\lambda t})$

$^{207}Pb/^{204}Pb = Y = b + V(1-e^{\lambda' t})$

$^{208}Pb/^{204}Pb = Z = c + W(1-e^{\lambda'' t})$

Using the software modelling, the constants of $\lambda = 0.155125 \times 10^{-9}\ yr^{-1}$, $\lambda' = 0.155125 \times 10^{-9}\ yr^{-1}$, $\lambda'' = 0.155125 \times 10^{-9}\ yr^{-1}$, $\alpha = {}^{238}U/{}^{235}U = 137.88$ were inserted to solve the chemical formula. The result showed the corrected values from modification in the values of Pb isotope ratios, as follows: a = 18.465 ± 0.074, b = 15.642 ± 0.010 and c = 38.057 ± 0.095, whereas V = 0.066413 ± 0.00085 and W = 36.058 ± 0.13.

The calculated of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ values vs the assumption time as list in Table 2 are plotted in Figure 1.

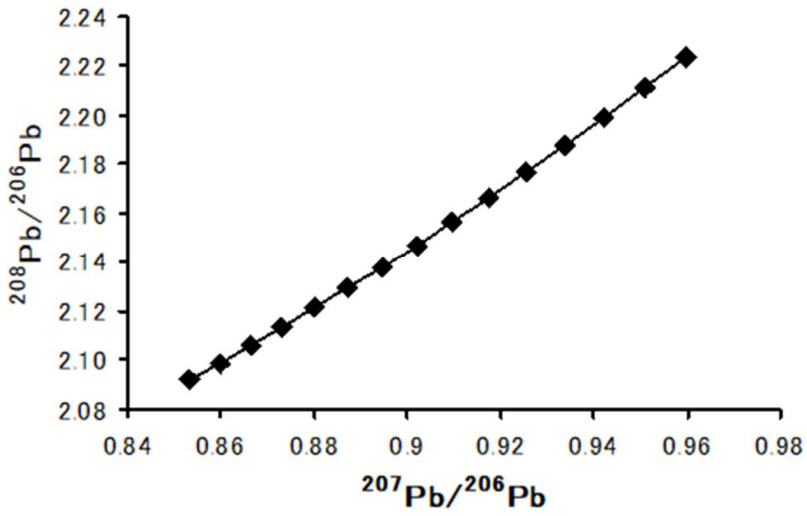

Figure 1 $^{208}Pb/^{206}Pb$ vs. $^{207}Pb/^{206}Pb$ plots in the Pb growth of curve

Figure 1 shows the lower of $^{208}Pb/^{206}Pb$ vs. $^{207}Pb/^{206}Pb$ indicates the recent mine or ores with the present day and the high values of them reflected the oldest mine. The Pb-growth curved was made in the mine of the ore, which considered as the part of content in media samples. This figure provided the finger print of mine inside with the relation with time of its age. The line of this figure, it indicates by Pb pollution contained the mine, which contribute the high of level Pb concentration.

3. Results and Discussion

3.1 Application of Lead growth Curved for Identification of Pb

Application of Pb growth curved is very important to detect the source of anthropogenic and natural inputs with all samples contained Pb. The group of samples were

categorized with group anthropogenic or natural depending the values of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$. The characterized of sample group anthropogenic and natural sources cannot be changed with chemical fractionations of Pb. The measurements of Pb isotopes using ICP-MS (Inductivelly Coupled Plasma-Mass Spectrometry) always are depended the concentration of Pb. When we knew the concentration of Pb, the process dilution of Pb should be the same with the standard concentrations of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ (~10 ppb) for all samples. Using ICP-MS, it measures the ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb and then corrects their mass bias with SRM (Standard Reference Material) after every two samples.

All investigated samples were measured of Pb concentratios using ICP-MS and then continued to measure the reference of anthropogenic and natural sources with the same procedures. All of investigated samples and the reference should content of Pb concentations for continuing the Pb isotope measurements. The content of Pb and its Pb isotope ratios in the ancient of samples were changed by modern of Pb-anthropogenic. For example, the range of Pb isotope ratios of the river sediment, road-side dust, seawater were recorded, as follows: $^{208}Pb/^{206}Pb$: 2.075–2.113 and $^{207}Pb/^{206}Pb$: 0.834–0.868, $^{207}Pb/^{206}Pb$ = 0.8644–0.8688 and $^{208}Pb/^{206}Pb$ = 2.1044–2.170, and $^{207}Pb/^{206}Pb$ = 0.7966-0.9945 and $^{208}Pb/^{206}Pb$ = 2.2600-2.8243 [4–6]. As shown in Figure 2, there are 3 groups for the finger print of Pb isotope ratios of sediment, road-side dust and seawater samples, respectivelly. Pb concentrations in road-side dust contaminated the part of sediment and seawater samples. In order to understand of the source of Pb, we plotted the another media samples, which suspected the anthropogenic and natural sources surrounding sampled locations.

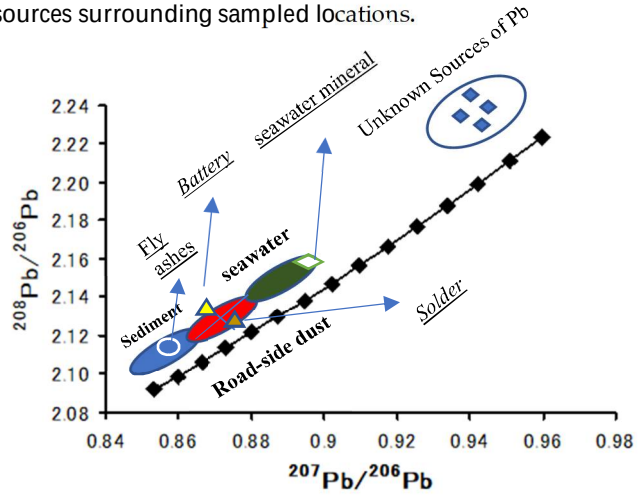

Figure 2. Application of $^{208}Pb/^{206}Pb$ vs $^{207}Pb/^{206}Pb$ in the Pb growth curved

The Pb isotope ratios of the sediment with lower ratios closes with the Pb isotope ratios of fly ash indicating the most of sediment contaminated by Pb-fly ash. This means it can support the policies government to recheck the sewage of industry surrounding the collected sediment. Sediment can reflect the contaminated of Pb. The sewage of industry released Pb-materials products such as Pb-battery, Pb solder, Pb-fly ash brick plant. The finger print of Pb isotope ratios in road-side dust clearly contributed from Pb-battery and Pb-solder (Figure 2). As shown in Figure 2, the Pb battery and solder can be considered by vehicles crossing the sampled road-side dust. All of electronic components from old vehicles is possibly as one factor releasing Pb to road-side dust.

Pb isotope ratios of seawater samples is more radiogenic comparing with those in sediment and road-side dust. The values of Pb isotopes of mine as compiler the Pb concentrations in seawater samples indicated the recient of Pb. The Pb concentration in seawater was released by mineral sources in seawater sediment and effected by anthropogenic inputs from river or urbanized areas. As shown in Figure 2, the dominated of Pb in seawater possibly was derivated from road-side dust. However, in the finger print of Pb in seawater was experienced the overlapping with Pb isotope ratios of seawater mineral. Seawater mineral was derivated from lithogenic or natural sources in marine sediment. The Pb in marine sediment was leached by acid condition of seawater when it is effected by acid rain or abundance of sewage from urbanized areas.

As shown in Figure 2, some samples falled out from the growth curved and reference materials indicating unknown sources. The unknown source of Pb samples indicates the new mine or modern mine and do not have the specific characters or mineralogical of Pb. We need more explore of Pb surrounding collected samples which mineral suspected to nearly contribute Pb in media samples.

Figure 2 also shows the useful of Pb isotope ratios of two kind samples such as road-side dust and sediment were tended to Pb-anthropogenic and seawater sample was effected by natural sources. The Pb-anthropogenic samples are identified by Pb-pollution and output of this research is to support policies government. However, the Pb-natural sources was shown by Pb isotope ratios of seawater can be used the local people and researcher increase the shrimp and fisheries productivities [6,9]. They can more explore the physico-chemical characteristics to support the potensial area. Wijaya et al. [6] reported that the positive correlation between the natural of Pb isotope ratios in seawater with clorophyll *a* and the values of DO, BOD, COD, pH, and temperature were determined in accordance with their values of WHO (World Health Organization).

In order to confirm the value of Pb isotope ratios of samples contributed by natural source, we can continue to measure ^{238}U, ^{235}U, and ^{232}Th by ICP-MS (Figure 3). Measuring of U and Th were measured in the same media sample and then modified as $^{238}U/^{235}U$ and

$^{232}Th/^{235}U$. The positive correlation of $^{208}Pb/^{206}Pb$ vs $^{238}U/^{235}U$ and $^{207}Pb/^{206}Pb$ vs $^{232}Th/^{235}U$ were shown in Figures 3a and b indicating the positive of Pb source from parents rock. As shown in Figure 3, the increasing of values of $^{208}Pb/^{206}Pb$ was followed by values of $^{238}U/^{235}U$ with R^2 0.8344. It suggests the natural sources of the daughter of ^{208}Pb, ^{206}Pb originated by parents rock ^{238}U and ^{235}U. When the correlation of those was less than 0.45, it was possibly contaminated by Pb-anthropogenic inside due to the overlapping of Pb values.

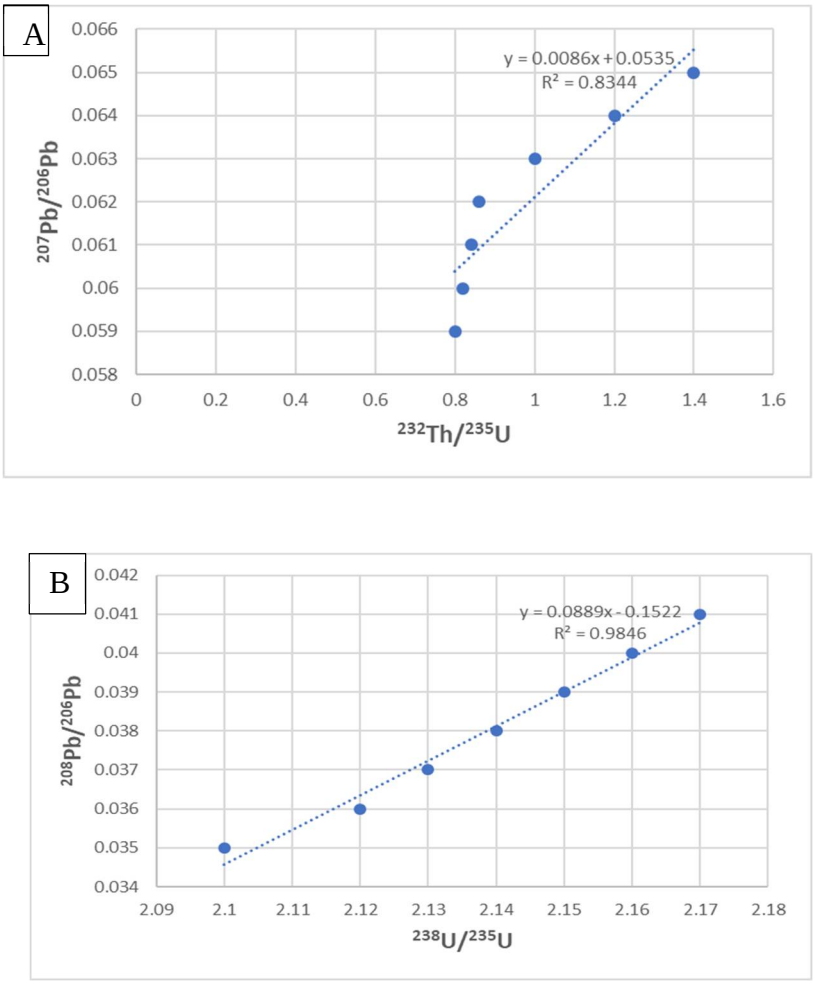

Figure 3 Relationship between (a) $^{208}Pb/^{206}Pb$ vs $^{238}U/^{235}U$ (b) and $^{207}Pb/^{206}Pb$ vs $^{232}Th/^{235}U$.

In case of $^{207}Pb/^{206}Pb$, the positive correlation with $^{232}Th/^{235}U$ was also shown in Figure 3b. ^{207}Pb, ^{206}Pb indicated from the parent rocks from ^{232}Th, and ^{235}U, respectivelly. The pattern of $^{207}Pb/^{206}Pb$ vs $^{232}Th/^{235}U$ differed with $^{208}Pb/^{206}Pb$ vs $^{238}U/^{235}U$. A little change of pattern of $^{232}Th/^{235}U$ indicates the slowly decay from parent rocks (0.800-0.900). As shown in Figure 3a, the both of positive correlation of $^{207}Pb/^{206}Pb$ vs $^{232}Th/^{235}U$ and $^{208}Pb/^{206}Pb$ vs $^{238}U/^{235}U$ reflected the pure of Pb-natural sources. When one of those has the negative correlation between their correlation indicates the mixture of Pb natural and anthropogenic sources.

Conclusion

Detection using Pb isotope ratios were started to calculate Pb concentrations of samples. Pb concentrations were then changed by ^{208}Pb, ^{206}Pb, ^{207}Pb and ^{204}Pb to establish accuracy and precision of $^{208}Pb/^{206}Pb$ vs $^{207}Pb/^{206}Pb$. The value of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ of samples were plotted with the lead growth curved. The overlapping of the values isotope ratios of samples with anthropogenic and natural references indicates the samples come from anthropogenic or natural inputs.

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