

Evaluation of lead isotope compositions of NIST NBS 981 measured by thermal ionization mass spectrometer and multiple-collector inductively coupled plasma mass spectrometer

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Abstract

Because Pb isotopes can be used for tracing, they are widely used in many disciplines. The detection and analysis of Pb isotopes of bulk samples are usually conducted using thermal ionization mass spectrometer (TIMS) and multiple-collector inductively coupled plasma mass spectrometer (MC-ICP-MS), both of which need external reference materials with known isotopic compositions to correct for the mass discrimination effect produced during analysis. NIST NBS 981 is the most widely used reference material for Pb isotope analysis; however, the isotopic compositions reported by various analytical laboratories, especially those using TIMS, vary from each other. In this study, we statistically evaluated 229 reported TIMS analysis values collected by GeoReM in the last 30 years, 176 reported MC-ICP-MS analysis values, and 938 MC-ICP-MS analysis results from our laboratory in the last five years. After careful investigation, only 40 TIMS results were found to have double or triple spikes. The ratios of the overall weighted averages, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$, obtained from 40 spiked TIMS reports and 1114 MC-ICP-MS results of NIST NBS 981 isotopes were 16.9406 ± 0.0003 (2s), 15.4957 ± 0.0002 (2s), and 36.7184 ± 0.0007 (2s), respectively.

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Keywords: NIST NBS 981; Lead isotope; Thermal ionization mass spectrometer; Multiple-collector inductively coupled plasma mass spectrometer; GeoReM

1. Introduction

Because of the unique geochemical properties of Pb, its isotopes can be used for various purposes such as tracing of different magmatic processes, ore-forming material sources, raw material sources of bronzeware and chinaware, and biological processes. Thus, Pb isotopes are widely applied in different fields, including earth sciences, archaeological science, material science, biological science, chemistry, and environmental science (Dreyfus et al., 2007; Kate Souders and Sylvester, 2008; Schultheis et al., 2004; Sjastad et al., 2011; Teresa de la Cruz et al., 2009). Accurate analysis of Pb isotopes is the prerequisite for these studies.

Abbreviations: ESA, electrostatic analyzer; ETV, electrothermal vaporization; IC, ion-counting multiplier; LA, laser ablation; MC-ICP-MS, multiple-collector inductively coupled plasma mass spectrometer; TIMS, thermal ionization mass spectrometer; PFA, perfluoroalkoxy.

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Currently, there are mainly three methods for Pb isotope analysis: secondary ionization mass spectrometer (SIMS), thermal ionization mass spectrometer (TIMS) and multiple-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) (Baker et al., 2004; Belshaw et al., 1998; Chen et al., 2014; Hirata, 1996; Ortega et al., 2012; Pomiès et al., 1998; Taylor et al., 2015; Whitehouse et al., 2005). The SIMS technique needed solid state reference materials for external calibration since it is an in situ analytical technique, and the Pb isotopic compositions of the solid state reference materials was normally ascertained by TIMS or MC-ICP-MS techniques. TIMS uses a thermal ionization ion source, has a stable ion production rate, and can achieve highly accurate Pb isotope composition when a double or triple spike is added, making it the preferred method for the certification of standard samples (Galer, 1999; Powell et al., 1998; Ruiz Encinar et al., 2001; Taylor et al., 2015). MC-ICP-MS uses ICP as the ion source and an interface composed of a sampler cone and skimmer cone. Both ICP and interface had a kinetic energy spread which led to a defocusing of the ion beam (Becker, 2007). Although the subsequent electrostatic analyzer (ESA) can compensate for the kinetic energy spread, the final Pb isotope accuracy is usually poorer than TIMS. However, the MC-ICP-MS has a simple sample preparation process, provides fast analysis speeds, and can be easily connected with third-party sample injection systems (such as desolvator, electrothermal vaporization (ETV), and laser ablation (LA)) to increase sensitivity and achieve in situ microanalysis. Additionally, the accuracy of the analysis meets the requirements of modern studies; therefore, MC-ICP-MS is commonly used in mainstream Pb isotope analysis. Unlike TIMS that corrects quality discrimination of MS by adding spikes, MC-ICP-MS uses an external reference (NIST NBS 981 is commonly used) or a combination of external reference and internal isotope pairs (^{203}Tl and ^{205}Tl are commonly used because their mass numbers are close to that of Pb) to correct the mass discrimination of MS, so as to achieve an accuracy of analysis that is approaching TIMS measurement using double or triple spikes (Taylor et al., 2015).

Many laboratories have analyzed and reported the Pb isotopic composition of NIST NBS 981. We compared all the reported data included in the GeoReM database (<http://georem.mpch-mainz.gwdg.de/>). A database for all kinds of reference materials and isotopic standards of geochemical and mineralogical interest up to May 2015 (Jochum et al., 2005), and found that the NIST NBS 981 ratios used by different laboratories as the external reference are not the same and that there are significant system deviations in TIMS analysis results. Since different laboratories use NIST NBS 981 as the external reference to obtain Pb isotopic compositions of their real samples, any difference in this reference value will directly affect the analytical accuracy of the real samples. Therefore, it is necessary to certify the NIST NBS 981 ratios, so that the Pb isotope ratios analyzed by different laboratories are comparable. Although some researchers have discussed Pb isotope ratios of NIST NBS 981, none of them has systematically analyzed the published reference ratios (Baker et al.,

2004; Collerson et al., 2002; De Muynck et al., 2008; Sarkar et al., 2015; Taylor et al., 2015; Todt et al., 1996).

In this study, Pb isotopic composition of NIST NBS 981 was statistically evaluated based on the composition obtained through MC-ICP-MS analyses at the State Key Laboratory of Continental Dynamics in the last five years, and by using previously reported TIMS and MC-ICP-MS results.

2. Experimental

2.1. Reagents and materials

Nitric acid (HNO_3) used in this study was purified twice through DST-1000 sub-boiling stills (Saville Corporation, Eden Prairie, MN USA). The ultrapure water (electrical conductivity $> 18.2 \text{ M}\Omega \text{ cm}^{-1}$) used in the experiment was produced by using a water purifier (Millipore, USA) and was further purified by using a quartz sub-boiling distiller. The Pb background concentration was $< 200 \text{ pg g}^{-1}$. Both NIST NBS 981 (Pb) and NIST SRM 997 (Tl) were purchased from the National Institute of Standards and Technology (NIST).

2.2. Instrumentation

All analyses were conducted at the State Key Laboratory of Continental Dynamics at Northwest University. Two MC-ICP-MSs (Nu Plasma I (NP-I) and Nu Plasma II (NP-II)) from Nu Instruments (Wrexham, UK) were used. NP-I has 12 F cups (FC) and 3 full-sized discrete dynode ion-counting multipliers (IC), while NP-II has 16 FCs and 5 ICs. ^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{202}Hg , ^{203}Tl , and ^{205}Tl isotopes were analyzed in static state using the FCs. ^{202}Hg was used to monitor the Hg level in the gas background, and to correct for the isobaric interference on ^{204}Pb according to the natural abundance ratio. The resistances of the pre-amplifiers were $10^{11} \Omega$. ^{203}Tl and ^{205}Tl were used to correct for the mass discrimination of Pb and Hg isotopes using exponential law ($^{205}\text{Tl}/^{203}\text{Tl} = 2.3889$, $^{204}\text{Hg}/^{202}\text{Hg} = 0.229883$) (Chen et al., 2014; Yuan et al., 2013). NIST NBS 981 (Pb) and NIST SRM 997 (Tl) were mixed at a Pb:Tl ratio of ~ 1 , and the mixture was then injected using two desolvators (DSN-100 for Nu Plasma I; Aridus II for Nu Plasma II). The nebulizer used was the PFA micro-flow nebulizer ($100 \mu\text{L min}^{-1}$). Sensitivities of NP-I and NP-II were larger than 300 and 600 V ppm^{-1} (total Pb beam), respectively. Instrument parameters are shown in Table 1.

2.3. Data source

We statistically analyzed the Pb isotope data collected by the GeoReM website from published papers in the last 30 years (Jochum et al., 2005), as well as Pb isotopic compositions obtained through MC-ICP-MS analyses at the State Key Laboratory of Continental Dynamics in the last five years, and three reported TIMS results with lead spikes that were not present in GeoReM bibliographic lists (Galer, 1998; Hamelin et al., 1985; Thirlwall, 2000; Woodhead et al., 1995). GeoReM has collected NIST 981 data from 1985 to 2015, including 229

Table 1
Instrumental parameters for MC-ICP-MSs (Nu Plasma I and II).

MC-ICP-MS	Nu plasma I	Nu plasma II
RF power, W	1300	1300
Coolant gas flow, L min ⁻¹	13	17
Auxiliary gas flow, L min ⁻¹	0.8	0.8
Nebulizer gas flow, psi	32–38	32–35
Acceleration voltage	4000	6010
Dry plasma sensitivity, V ppm ⁻¹	300	600
Faraday cup setup	²⁰⁸ Pb(H ₄), ²⁰⁷ Pb (H ₃), ²⁰⁶ Pb (H ₂), ²⁰⁵ Tl (H ₁), ²⁰⁴ (Pb + Hg) (Ax), ²⁰³ Tl (L1), ²⁰² Hg (L2)	²⁰⁸ Pb(H ₂), ²⁰⁷ Pb (H ₁), ²⁰⁶ Pb (Ax), ²⁰⁵ Tl (L1), ²⁰⁴ (Pb + Hg) (L2), ²⁰³ Tl (L3), ²⁰² Hg (L4)
Faraday cup voltage, V	0–10	0–50
Blank acquisition, s	30	30
Integrated time per measurement, s	8	8
No. of measurements per block	20	20
No. of blocks	3	3
Desolvator	DSN-100	Aridus II

TIMS analysis results and 176 MC-ICP-MS analysis results from 58 institutes. [Supplementary Table 1](#) lists the names of these institutes, corresponding GeoReM paper IDs, and used analytical methods.

3. Results and discussions

3.1. TIMS results (based on GeoReM data source)

GeoReM contains 229 Pb isotope reports from 58 laboratories around the world, including 208 ²⁰⁶Pb/²⁰⁴Pb reports, 202 ²⁰⁷Pb/²⁰⁴Pb reports, and ²⁰⁸Pb/²⁰⁴Pb reports, among which only the ratios with uncertainties were evaluated (191 ²⁰⁶Pb/²⁰⁴Pb reports, 185 ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb reports). The isotope ratio distributions of ²⁰⁸Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb over ²⁰⁶Pb/²⁰⁴Pb (Fig. 1) revealed two regions in TIMS analysis results (Groups A and B in both Fig. 1a and b). In Group A, the weighted averages of the Pb isotope ratios ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb were 16.8912 ± 0.0016 (2s, n = 90), 15.4292 ± 0.0020 (2s, n = 88), and 36.5152 ± 0.0072 (2s, n = 88), respectively. In Group B, the weighted averages of the Pb isotope ratios ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb were 16.9400 ± 0.0007 (2s, n = 101), 15.4979 ± 0.0008 (2s, n = 97), and 36.7208 ± 0.0033 (2s, n = 97), respectively. Isotope ratios of Group A were significantly lower than those of Group B (Fig. 1). Although the analytical accuracy of TIMS has improved by one order of magnitude in the last 20 years (Taylor et al., 2015), the correlation coefficients between Pb isotope ratios ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb and their respective publishing years were 0.13, 0.15, and 0.15 (Fig. 2), suggesting no correlation between the accuracy of the TIMS analyses and the progress of TIMS analytical technology. The relative deviations of the two groups are 0.29%, 0.45%, and 0.56% for the ratios ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb, respectively. Pb isotope ratios of Groups A and B (Fig. 1) do not fall within the error range, suggesting the presence of system deviations between the reported TIMS ratios. The offset of Group A from Group B could be caused by different correction method applied to calibrate mass discrimination. The

Group A represents those TIMS results without spiked calibration method, while Group B represents those reports adopted spiked calibration method. Since the double or triple spiked method can calibrate the mass discrimination of TIMS effectively, Group B could represent TIMS analyses.

Only 40 ²⁰⁶Pb/²⁰⁴Pb results and 38 ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb reports (Fig. 1) were analyzed by the double- or triple-spiked method among the 237 reported TIMS results,

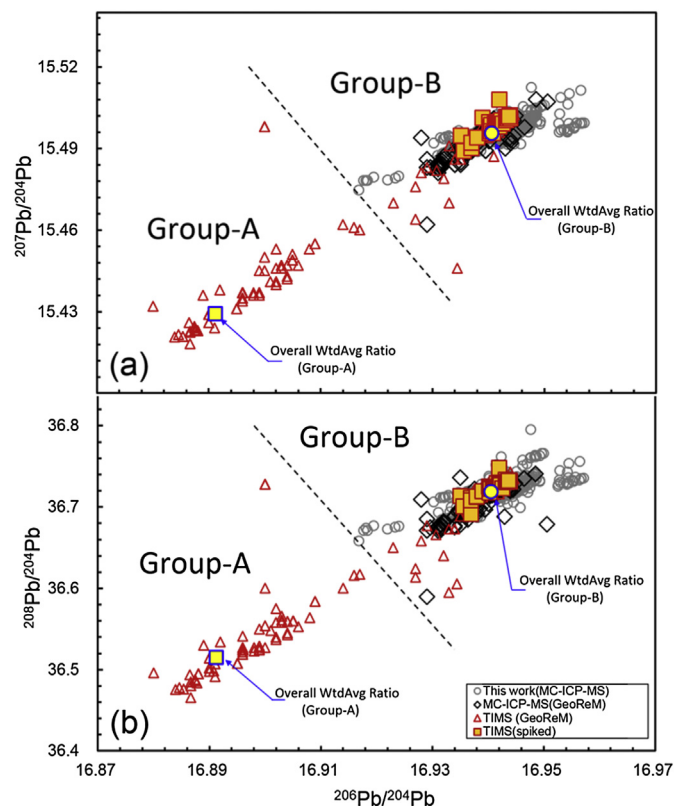


Fig. 1. Distributions of Pb isotopes ²⁰⁷Pb/²⁰⁴Pb–²⁰⁶Pb/²⁰⁴Pb, ²⁰⁸Pb/²⁰⁴Pb–²⁰⁶Pb/²⁰⁴Pb from GeoReM dataset (TIMS (the triangle) and MC-ICP-MS (the diamond)) and this study (NWU results, the circle). Group A and Group B represent TIMS analyses without and with spiked method calibration, respectively.

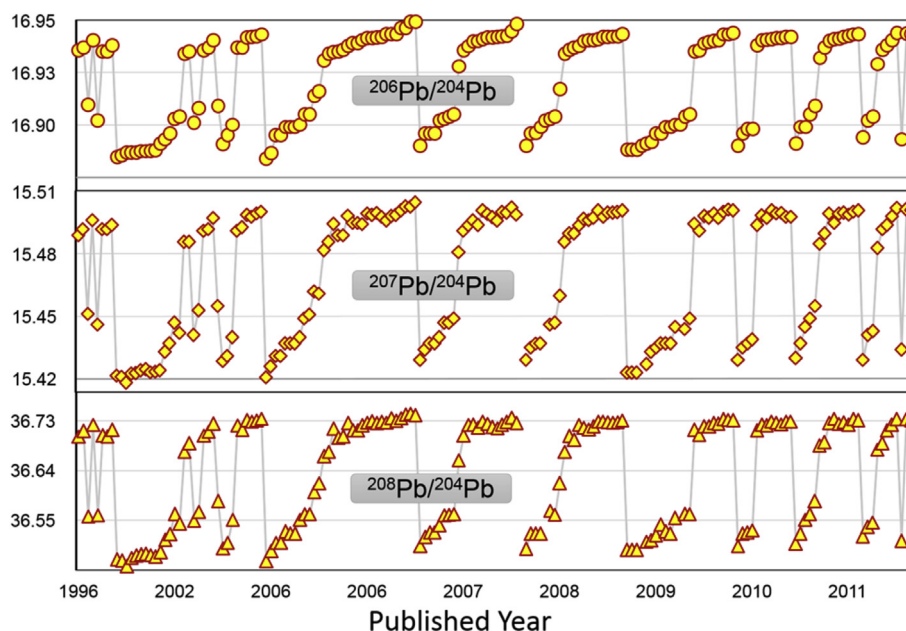


Fig. 2. Trend of TIMS-analyzed $^{207}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ ratios included in the GeoReM website over time (1996–2015).

while the others were reported after normalizing to reference Pb ratios by spiked analyses. The weighted average of the 40 $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, 38 $^{207}\text{Pb}/^{204}\text{Pb}$, and 38 $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of lead-spiked TIMS results are 16.9413 ± 0.0006 , 15.4992 ± 0.0008 , and 36.7259 ± 0.0020 , respectively.

3.2. MC-ICP-MS results (based on GeoReM data source and results of author's laboratory)

Since the fractionation effects of instruments are constant over time during MC-ICP-MS analysis, accurate isotope ratios can be obtained after correcting for fractionation with a proper correction strategy. TI has a mass number close to that of Pb, and therefore, it is mainly used for the fractionation correction of MS in the MC-ICP-MS analysis of Pb isotopes. There were 176 ICP-MS reports in the published GeoReM database, of which there were 157 $^{206}\text{Pb}/^{204}\text{Pb}$ reports, and 152 $^{207}\text{Pb}/^{204}\text{Pb}$ and 152 $^{208}\text{Pb}/^{204}\text{Pb}$ reports with errors, and their weighted averages were 16.9407 ± 0.0010 (2s, $n = 157$), 15.4950 ± 0.0009 (2s, $n = 152$), and 36.6981 ± 0.0031 (2s, $n = 152$), respectively, all belonging to Group B shown in Fig. 1. In our laboratory, the NIST NBS 981 was dissolved using a chemical method, and TI was added to correct for the mass discrimination effect of MC-ICP-MS during Pb isotope analysis, which has been conducted 938 times in the last five years. The two MC-ICP-MSs afford similar accuracy and precision of Pb isotope analysis. The weighted averages of the $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of the two systems were 16.9410 ± 0.0003 , 15.4959 ± 0.0002 , and 36.7208 ± 0.0005 (2s, $n = 938$), respectively, all belonging to Group B shown in Fig. 1. By comparing the weighted averages between our laboratory and GeoReM, the relative deviations of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios were found to be 0.016%, 0.0058%, and 0.062%, respectively.

3.3. Recommended results

Taylor et al. (2015) comprehensively evaluated the analysis results of different mass spectrometers over 18 years, and conducted comparative analyses on external correction methods for instrumental fractionation, such as thallium spiking, sample-standard bracketing, and double/triple spiking. The obtained working ratios of NIST 981 Pb were 16.9412, 15.4988, and 36.7223 for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$, respectively. All these isotope ratios belong to Group B of the GeoReM data (Fig. 1). After combining 938 analysis results of our laboratory, 152–157 MC-ICP-MS results of GeoReM, and 40–38 TIMS data after lead spiking, the weighted averages of the Pb isotope ratios $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ were found to be 16.9406 ± 0.0003 (2s, $n = 1135$), 15.4957 ± 0.0002 (2s, $n = 1128$), and 36.7184 ± 0.0007 (2s, $n = 1128$), respectively.

These results were obtained through 30 years of analyses conducted by different laboratories. As a result, use of weighted averages is recommended based on the analysis of all MC-ICP-MS and TIMS results as benchmark ratios for different laboratories for future instrument calibrations.

4. Conclusions

In this paper, the results of NIST NBS 981, including 938 MC-ICP-MS analyses conducted by our laboratory in the last five years, and 229 TIMS and 176 MC-ICP-MS analyses published and included in the GeoReM website, were statistically analyzed. There were apparently two distribution regions of the reported NBS 981 values analyzed by TIMS, and the results of lead-spiked analysis by TIMS overlapped with MC-ICP-MS analysis. The weighted averages of the Pb isotope ratios $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ in this

overlapped region (including all MC-ICP-MS results and TIMS results with Pb spiking) were 16.9406 ± 0.0003 (2s, $n = 1135$), 15.4957 ± 0.0002 (2s, $n = 1128$), and 36.7184 ± 0.0007 (2s, $n = 1128$), respectively. All laboratories are recommended to use these ratios as reference for future Pb isotope analyses, so as to eliminate the possible system errors when performing Pb isotope analysis in different laboratories.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.sesci.2016.04.001>.

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