



COMMENT

10.1002/2015GC005914

This article is a comment on *J.-I. Kimura et al.* [2014], doi:10.1002/2013GC005132.

Correspondence to:

E. Nakamura,
eizonak@misasa.okayama-u.ac.jp

Citation:

Pineda-Velasco, I., T. T. Nguyen, H. Kitagawa, and E. Nakamura (2015), Comment on "Diverse magmatic effects of subducting a hot slab in SW Japan: Results from forward modeling" by J.-I. Kimura et al., *Geochem. Geophys. Geosyst.*, 16, 2848–2852, doi:10.1002/2015GC005914.

Received 15 MAY 2015

Accepted 13 JUL 2015

Accepted article online 16 JUL 2015

Published online 30 AUG 2015

Comment on "Diverse magmatic effects of subducting a hot slab in SW Japan: Results from forward modeling" by J.-I. Kimura et al.

Ivan Pineda-Velasco¹, Tai T. Nguyen¹, Hiroshi Kitagawa¹, and Eizo Nakamura¹

¹Pheasant Memorial Laboratory, Institute for Study of the Earth's Interior, Okayama University, Misasa, Japan

1. Introduction

The recently published paper by *Kimura et al.* [2014] reports geochemical and isotopic analyses of Quaternary adakitic dacites (ADK) from two volcanic groups, Daisen and Aonoyama, in southwest (SW) Japan (Figure 1). Based on Pb isotope compositions, these authors suggest that crustal assimilation played a major role in the genesis of ADK. This conclusion differs from that of an earlier study by *Feineman et al.* [2013], who advocated only a minimal crustal effect and concluded that the Pb isotope array for Daisen ADK can be attributed to partial melting of the subducting slab with a significant amount of sediment. The Pb isotope trends for Daisen ADK presented in these two studies are clearly different (Figure 2) and *Kimura et al.* [2014] did not directly compare the data sets or provide any explanation for the differences.

In this comment, we critically examine the differences between the Pb isotope data sets presented by *Feineman et al.* [2013] and *Kimura et al.* [2014]. We present new data for Aonoyama ADK and we provide an explanation for the discrepancy between the data obtained in our lab and in this other recently published study.

2. Samples

2.1. Daisen

The samples used in *Feineman et al.* [2013] and *Kimura et al.* [2014] were collected from the main peaks around Misen at Daisen volcano [see *Feineman et al.*, 2013, Figure 1]. In *Kimura et al.* [2014], ADK from the Hiruzen mountains, located 10 km southeast of Misen, are also included ($n = 2$). Data in *Kimura et al.* [2014] labeled as being for "Daisen" and "Karasugasen" ($n = 12$) are used in our evaluation. The major-element compositions for Daisen volcanics presented by *Kimura et al.* [2014] and obtained in our study, show great overlap (Table 1), thus large differences in the isotopic compositions for the sample suites investigated in the two studies would not be anticipated.

2.2. Aonoyama

We present new data for ADK from 14 lava domes in the Aonoyama chain, containing four volcanoes (Aonoyama, Sengokudake, Tokuyamamitakesan, and Dakeyama), allowing direct comparison of our data set with that of *Kimura et al.* [2014]. Major-element compositions we obtained for the Aonoyama ADK are essentially identical to those by *Kimura et al.* [2014] (see Table 2).

3. Analytical Methods

A double spike (DS) method [*Kuritani and Nakamura*, 2003], using thermal ionization mass spectrometry (TIMS), was applied in *Feineman et al.* [2013] and to obtain our new data presented here. *Kimura et al.* [2014] employed a TI-spiking (TS) technique employing multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) [*Kimura et al.*, 2010]. In our study, samples were leached with 6M HCl (at 100°C) prior to sample decomposition to eliminate potential contamination and secondary alteration. During the analytical campaign, NBS 981 ($n = 10$) yielded an average of 16.9418 (14) for $^{206}\text{Pb}/^{204}\text{Pb}$, 15.4995 (19) for $^{207}\text{Pb}/^{204}\text{Pb}$, 36.7261 (47) for $^{208}\text{Pb}/^{204}\text{Pb}$ (2σ variability on last digits in parentheses). Major-element abundances of the Aonoyama ADK were obtained by X-ray fluorescence spectrometry, as outlined in *Feineman et al.* [2013].

© 2015. The Authors.

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

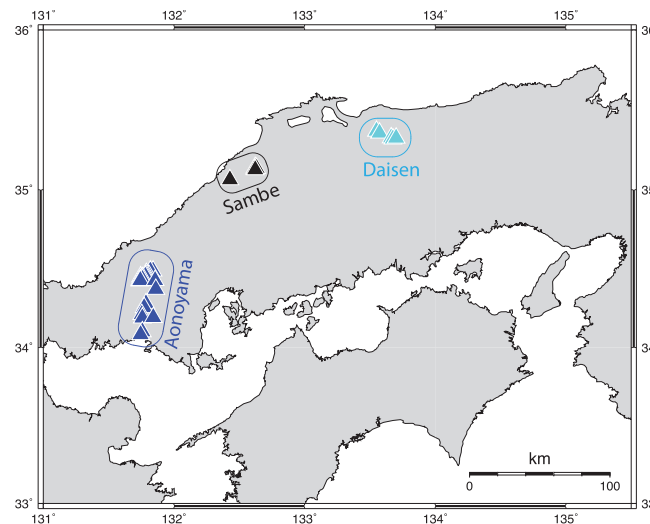


Figure 1. Distribution of the adakitic volcanoes in SW Japan [Nishiki *et al.*, 2012]. Colored triangles show the volcanic peaks in each area: lightblue, Daisen group; black, Samba group; darkblue, Aonoyama group. The basemap is created using GMT [Wessel *et al.*, 2013].

4. Discrepancy of Pb Isotope Data

Figure 2 demonstrates the differences between the Pb isotope data sets obtained in our laboratory [Feineman *et al.*, 2013, this study] and by Kimura *et al.* [2014]. The data from Kimura *et al.* [2014] show steeper trends in $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{208}\text{Pb}/^{204}\text{Pb}$ plots than those observed by Feineman *et al.* [2013] and in our more recent study.

Discrepancies in the Pb isotope data obtained by DS and TS methods have previously been discussed [e.g., Thirlwall, 2002; Baker *et al.*, 2004]. For example, Baker *et al.* [2004] demonstrated that analyses by DS methods differ by 3000 ppm

from those obtained by TS methods for Icelandic picrite [Stracke *et al.*, 2003]. Baker *et al.* [2004, 2005] suggested that this discrepancy could reflect (1) inadequate correction of instrumental mass bias using the TS methods, (2) unusual isotopic fractionation induced by excessive matrix load, and (3) contamination by Pb added to the samples both in the field and in the laboratory. In both studies, Pb blanks were reported as being less than 50 pg, and therefore negligible compared with the quantities of Pb analyzed (>100 ng).

Uncertainty in Pb isotope analysis tends to be largely to (1) mass bias and (2) error in measurement of ^{204}Pb [Hamelin *et al.*, 1985; Powell *et al.*, 1998; Thirlwall, 2000; Kuritani and Nakamura, 2003; Taylor *et al.*, 2015]. The mass bias effect can be approximated as a linear function [Hamelin *et al.*, 1985],

$$R = R_m(1 + \epsilon\Delta M) \quad (1)$$

where R_m and R are the measured and true isotope ratios, and ΔM is the mass difference between two isotopes, and ϵ is the mass discrimination coefficient per mass unit. Using the equation (1), the slope (m) of the mass bias effect in $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$ or $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{208}\text{Pb}/^{204}\text{Pb}$ diagrams is calculated as

$$m_{\text{mass bias}} = \frac{\Delta M_2 R_2}{\Delta M_1 R_1} \quad (2)$$

where R_1 is $^{206}\text{Pb}/^{204}\text{Pb}$ ($\Delta M_1=2$) and R_2 is $^{207}\text{Pb}/^{204}\text{Pb}$ ($\Delta M_2=3$) or $^{208}\text{Pb}/^{204}\text{Pb}$ ($\Delta M_2=4$). The ^{204}Pb -error line has a slope $m_{^{204}\text{Pb error}}$ [Powell *et al.*, 1998] calculated as

$$m_{^{204}\text{Pb error}} = \frac{R_2}{R_1} \quad (3)$$

Data sets obtained by Feineman *et al.* [2013] and in our study form a trend subparallel to the ^{204}Pb -error line, on a plot of $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$, but shows significantly shallower slope in $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$ (Figure 2). In contrast, the data for Daisen ADK from Kimura *et al.* [2014] follow the trend defined by mass bias. Also, tie lines connecting the data for each dome in Aonoyama group, presented by Kimura *et al.* [2014] and in our studies, are subparallel to the trend for mass bias (the one exception is for the data for Dakeyama). This observation is suggestive that the Pb isotope data presented in Kimura *et al.* [2014] are inaccurate due to an inadequate correction of instrumental mass bias.

We note that the separation chemistry employed by Kimura *et al.* [2014] involves a single-column pass [cf. Kimura *et al.*, 2003] that cannot sufficiently eliminate impurities [Baker *et al.*, 2005; Kuritani and Nakamura, 2002]. A number of studies have documented that the TI-correction for mass bias is compromised by excessive matrix loads inducing different behavior of Pb and Tl during sample introduction through nebulization

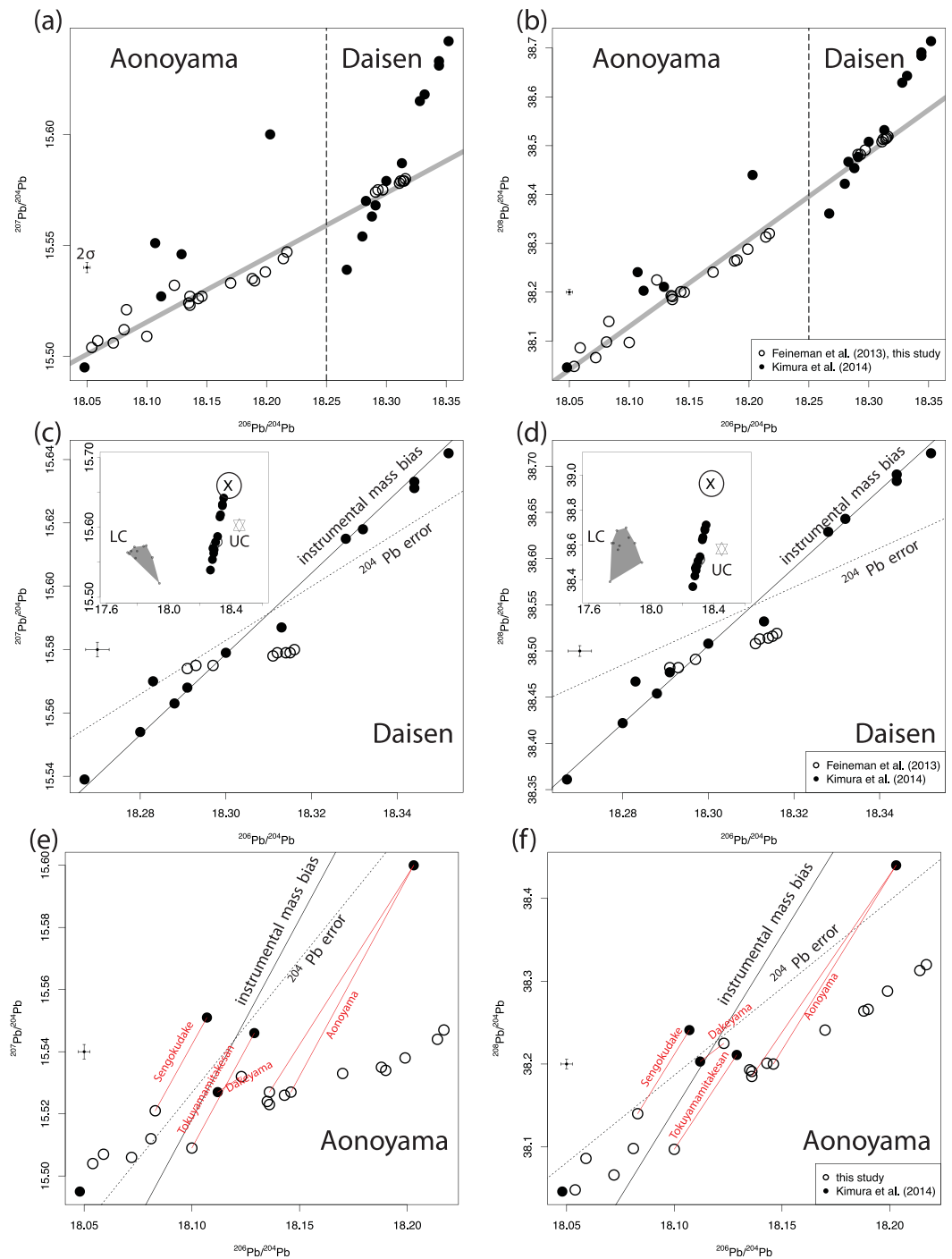


Figure 2. Pb isotope composition of ADK from Daisen and Aonoyama, obtained by *Feineman et al.* [2013], and this study, in comparison with those obtained by *Kimura et al.* [2014]. (a and b) Two volcanic groups plot in separated regions divided at $^{206}\text{Pb}/^{204}\text{Pb}$ 18.25. Data sets in *Feineman et al.* [2013] and obtained in this study show a trend shallower than that produced by the data in *Kimura et al.* [2014]. Note that our studies revealed that two ADK suites share a common linear trend (grey line). (c and d) Comparison of data sets for Daisen ADK. Compositions of upper crustal (UC) [*Feineman et al.*, 2013] and lower crustal (LC) [*Moriyama, 2006*] lithologies are shown in the insets. The “X” indicates the hypothetical crustal component suggested by *Kimura et al.* [2014]. (e and f) Comparison of data sets for Aonoyama ADK. The trajectories of instrumental mass bias and ^{204}Pb error are shown in Figures 2c and 2d as solid and dotted black lines, respectively. Each line passes through the mean of *Kimura et al.*'s [2014] data. Red tie-lines connect data for the same lava domes in the Aonoyama volcanic group. The slopes of these tie-lines are similar to the slope representing instrumental mass bias (the one exception is for the data for Daikayama). Analytical uncertainty (150 ppm) in our study is shown as error bars on the left side of each plot.

Table 1. Comparison of Major-Element (SiO₂ and K₂O) Abundances (on a Water-Free Basis) and Pb Isotope Compositions of Daisen ADK in *Feineman et al.* [2013] and *Kimura et al.* [2014]

Sample No.	Latitude (°N)	Longitude (°E)	SiO ₂ (wt.%)	K ₂ O (wt.%)	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb
<i>Feineman et al.</i> [2013]							
3060604	35.403	133.589	65.4	1.42	18.293	15.575	38.482
3052002	35.355	133.555	65.8	1.83	18.311	15.578	38.508
3052004	35.354	133.555	65.9	1.85	18.312	15.579	38.513
3052803	35.348	133.580	64.9	2.04	18.297	15.575	38.491
SAN2	35.377	133.572	65.2	2.15	18.291	15.574	38.482
2060707	35.364	133.538	65.8	1.79	18.314	15.579	38.514
2060710	35.364	133.538	65.7	1.74	18.316	15.580	38.519
2060711	35.364	133.538	65.7	1.74	18.315	15.579	38.516
<i>Kimura et al.</i> [2014]							
DS-15	–	–	65.1	2.09	18.291	15.568	38.477
DS99-2	–	–	65.9	1.76	18.283	15.570	38.467
DS99-3	–	–	63.6	0.70	18.267	15.539	38.361
033002-1	–	–	64.8	1.85	18.313	15.587	38.532
1-2	–	–	65.1	2.05	18.300	15.579	38.508
2-2	–	–	64.5	2.08	18.288	15.563	38.454
3-1	–	–	64.3	2.05	18.344	15.633	38.691
5-1'	–	–	65.1	1.94	18.344	15.631	38.684
5-2	–	–	64.3	2.19	18.332	15.618	38.643
6-2	–	–	63.8	1.96	18.280	15.554	38.422
7-1	–	–	65.5	2.05	18.352	15.642	38.714
8-1	–	–	63.8	1.92	18.328	15.615	38.629

and desolvation [Thirlwall, 2002; Kamenov et al., 2004]. Complete removal of matrix loads by double-column methods is crucial for obtaining precise and accurate Pb isotope analysis by both MC-ICPMS and TIMS [Woodhead, 2002; Baker et al., 2004].

5. Crustal Composition

Kimura et al. [2014] estimated the composition of crustal component by convergence of the Pb isotope arrays for the Daisen and Aonoyama groups (“X” in insets of Figures 2c and 2d). However, the composition

Table 2. Comparison of Pb Isotope Composition and Major-Element Abundances (on a Water-Free Basis) of Aonoyama ADK Obtained in This Study and by *Kimura et al.* [2014]

Sample No. (Lava Dome)	Latitude (°N)	Longitude (°E)	SiO ₂ (wt.%)	K ₂ O (wt.%)	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb
<i>This Study</i>							
AON-03 (Chikurayama)	34.494	131.814	65.0	1.61	18.170	15.533	38.241
AON-04 (Aonoyama)	34.473	131.800	65.2	1.52	18.146	15.527	38.200
AON-05 (Aonoyama)	34.472	131.796	64.7	1.54	18.136	15.527	38.185
AON-06 (Bentenyama)	34.467	131.786	61.2	1.44	18.136	15.523	38.191
AON-07 (Karekiyama)	34.464	131.783	63.5	1.83	18.135	15.524	38.193
AON-08 (Tai-insan)	34.441	131.765	64.1	1.92	18.188	15.535	38.264
AON-09 (Tai-insan)	34.448	131.765	64.5	1.94	18.190	15.534	38.266
AON-10 (Tai-insan)	34.442	131.764	63.0	1.37	18.199	15.538	38.288
AON-11 (Tai-insan)	34.448	131.762	64.5	1.85	18.143	15.526	38.201
AON-12 (Tai-insan)	34.448	131.758	64.1	1.72	18.217	15.547	38.320
AON-13 (Kumoimine)	34.444	131.744	64.6	1.85	18.214	15.544	38.313
AON-14 (Mottagadake)	34.378	131.869	57.9	1.40	18.072	15.506	38.066
AON-16 (Maruyama)	34.281	131.786	61.0	2.03	18.081	15.512	38.098
AON-17 (Dakeyama)	34.076	131.751	63.6	2.41	18.123	15.532	38.225
AON-18 (Shikumagadake)	34.098	131.761	61.9	2.35	18.054	15.504	38.048
AON-20 (Tokuyamamitakesan)	34.187	131.833	65.5	2.04	18.100	15.509	38.097
AON-21 (835 peak)	34.254	131.774	62.4	2.13	18.059	15.507	38.086
AON-22 (Sengokudake)	34.188	131.764	59.9	2.30	18.083	15.521	38.140
<i>Kimura et al.</i> [2014]							
AO-3 (Aonoyama)	–	–	64.8	1.51	18.203	15.600	38.440
SI-1 (Shiraidake)	–	–	59.6	2.55	18.048	15.495	38.046
SE-1 (Sengokudake)	–	–	60.8	2.13	18.107	15.551	38.241
MI-1 (Tokuyamamitakesan)	–	–	65.1	2.05	18.129	15.546	38.211
TA-2 (Dakeyama)	–	–	61.8	2.25	18.112	15.527	38.203

estimated by this approach is clearly distinct from the measured compositions for both upper and lower-crustal lithologies collected in the vicinity of Daisen volcano [Moriyama, 2006; Feineman et al., 2013].

6. Concluding Remarks

Based on our critical examination, we conclude that the Pb isotope data sets published by Kimura et al. [2014] are inaccurate due to erroneous correction for instrumental mass bias. The apparent convergence of the Pb isotope arrays [Kimura et al., 2014, Figure 7] to what these authors regard as a “common crustal component” is simply an artifact. The Pb isotope compositions of appropriate crustal rocks, presented by Moriyama [2006] and Feineman et al. [2013] indicate the nonavailability of crustal contaminants to deliver this hypothetical component beneath Daisen volcano. Our evaluation highlights the need for careful evaluation of the methods by which Pb isotope are obtained, as a number of factors can lead to erroneous data sets strongly affecting the conclusions reached.

Acknowledgments

We are grateful to Gray Bebout for improving the manuscript. All data for this paper are properly cited and referred to in the reference list. A map (Figure 1) was created using the Generic Mapping Tools [Wessel et al., 2013].

References

- Baker, J., D. Peate, T. Waight, and C. Meyzen (2004), Pb isotopic analysis of standards and samples using a ^{207}Pb – ^{204}Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS, *Chem. Geol.*, *211*(3–4), 275–303, doi:10.1016/j.chemgeo.2004.06.030.
- Baker, J. A., D. W. Peate, T. E. Waight, and M. F. Thirlwall (2005), Reply to the: Comment on “Pb isotopic analysis of standards and samples using a ^{207}Pb – ^{204}Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS” by Baker et al., *Chem. Geol.*, *217*(1–2), 175–179, doi:10.1016/j.chemgeo.2004.12.002.
- Feineman, M., T. Moriguti, T. Yokoyama, S. Terui, and E. Nakamura (2013), Sediment-enriched adakitic magmas from the Daisen volcanic field, Southwest Japan, *Geochem. Geophys. Geosyst.*, *14*, 3009–3031, doi:10.1002/ggge.20176.
- Hamelin, B., G. Manhès, F. Albarede, and C. J. Allègre (1985), Precise lead isotope measurements by the double spike technique: A reconsideration, *Geochim. Cosmochim. Acta*, *49*(1), 173–182, doi:10.1016/0016-7037(85)90202-9.
- Kamenov, G. D., P. A. Mueller, and M. R. Perfit (2004), Optimization of mixed Pb–Tl solutions for high precision isotopic analyses by MC-ICP-MS, *J. Anal. At. Spectrom.*, *19*, 1262–1267, doi:10.1039/B403222E.
- Kimura, J.-I., M. Kawahara, and S. Izumi (2003), Lead isotope analysis using TIMS following single column-single bead Pb separation, *Geosci. Rep. Shimane Univ.*, *22*, 49–53.
- Kimura, J.-I., A. J. R. Kent, M. C. Rowe, M. Katakuse, F. Nakano, B. R. Hacker, P. E. van Keken, H. Kawabata, and R. J. Stern (2010), Origin of cross-chain geochemical variation in Quaternary lavas from the northern Izu arc: Using a quantitative mass balance approach to identify mantle sources and mantle wedge processes, *Geochem. Geophys. Geosyst.*, *11*, Q10011, doi:10.1029/2010GC003050.
- Kimura, J.-I., et al. (2014), Diverse magmatic effects of subducting a hot slab in SW Japan: Results from forward modeling, *Geochem. Geophys. Geosyst.*, *15*, 691–739, doi:10.1002/2013GC005132.
- Kuritani, T., and E. Nakamura (2002), Precise isotope analysis of nanogram-level Pb for natural rock samples without use of double spikes, *Chem. Geol.*, *186*(1–2), 31–43, doi:10.1016/S0009-2541(02)00004-9.
- Kuritani, T., and E. Nakamura (2003), Highly precise and accurate isotopic analysis of small amounts of Pb using ^{205}Pb – ^{204}Pb and ^{207}Pb – ^{204}Pb , two double spikes, *J. Anal. At. Spectrom.*, *18*, 1464–1470, doi:10.1039/B310294G.
- Moriyama, T. (2006), Geochemical and isotopic study of lower crustal xenoliths from Oki-Dogo, southwest Japan: Implications for the origin and evolution of the continental lower crust, Ph.D. thesis, 203 pp., Graduate Sch. of Nat. Sci. and Technol., Okayama Univ., Okayama, Japan.
- Nishiki, K., J. Itoh, and T. Ueno (2012), Database of Quaternary volcanic and intrusive rock bodies in Japan, *Geol. Surv. Jpn. Interim Rep.*, *60*, Geol. Surv. of Jpn., The National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan.
- Powell, R., J. Woodhead, and J. Hergt (1998), Uncertainties on lead isotope analyses: Deconvolution in the double-spike method, *Chem. Geol.*, *148*(1–2), 95–104, doi:10.1016/S0009-2541(98)00023-0.
- Stracke, A., A. Zindler, V. J. M. Salters, D. McKenzie, J. Blichert-Toft, F. Albarède, and K. Grönvold (2003), Theistareykir revisited, *Geochem. Geophys. Geosyst.*, *4*(2), 8507, doi:10.1029/2001GC000201.
- Taylor, R. N., O. Ishizuka, A. Michalik, J. A. Milton, and I. W. Croudace (2015), Evaluating the precision of Pb isotope measurement by mass spectrometry, *J. Anal. At. Spectrom.*, *30*, 198–213, doi:10.1039/C4JA00279B.
- Thirlwall, M. F. (2000), Inter-laboratory and other errors in Pb isotope analyses investigated using a ^{207}Pb – ^{204}Pb double spike, *Chem. Geol.*, *163*(1–4), 299–322, doi:10.1016/S0009-2541(99)00135-7.
- Thirlwall, M. F. (2002), Multicollector ICP-MS analysis of Pb isotopes using a ^{207}Pb – ^{204}Pb double spike demonstrates up to 400 ppm/amu systematic errors in Tl-normalization, *Chem. Geol.*, *184*(3–4), 255–279, doi:10.1016/S0009-2541(01)00365-5.
- Wessel, P., W. H. F. Smith, R. Scharroo, J. Luis, and F. Wobbe (2013), Generic mapping tools: Improved version released, *Eos Trans. AGU*, *94*(45), 409–410, doi:10.1002/2013EO450001.
- Woodhead, J. (2002), A simple method for obtaining highly accurate Pb isotope data by MC-ICP-MS, *J. Anal. At. Spectrom.*, *17*, 1381–1385, doi:10.1039/B205045E.