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Short communication

Using the common-Pb standards SRM-981 and SRM-982 as double spikes

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Abstract

The two most widely used and well-documented common-Pb isotopic standards, SRM-981 and SRM-982, can be used as double spikes to correct for instrumental mass fractionation effects in TIMS data for a diverse range of radiogenic Pb samples.

Keywords: Pb isotopes; Mass fractionation; Double spike; SRM-981; SRM-982

1. Introduction

Thermal ionization mass spectrometric (TIMS) analysis of Pb is persistently affected by fractionation of the isotopes during ionization of the sample from the hot filament, and by the mass-dependent response of Daly or electron-multiplier ion detectors. The ratio perturbations are typically ~0.0015 amu^{-1} (0.15%) for single-filament ionization from a silica gel + H_3PO_4 matrix, using Faraday ion collectors. This combination is the most widely used, and is assumed in the following discussion, although the principles also apply to data acquired using other instruments. A first-order fractionation correction is often made to TIMS Pb/Pb data by applying a bias correction based on concurrent analyses of a standard material, most commonly SRM-981. In some laboratories, this is the only available remedy. As well as providing a correction factor, data for SRM-981 can be used to judge the variability in fractionation due to such things as load size, drying conditions and length of analysis, giving estimates of these components of the uncertainty in bias-corrected data. Values of ~±0.0005 amu^{-1} are often quoted for overall reproducibility. However, there are other differences between samples and standards, including residues from sample extraction and variable sample recovery (which limits estimation of load size), such that the performance of samples cannot be assumed to match the standards to high degree. Data quoted by Thirlwall [1] show that errors in bias-corrected data can be as large as the typical correction of 0.0015 amu^{-1}. It follows that, for at least some laboratories and some sample types, the real uncertainty in bias-corrected data is comparable to the correction applied, and ~0.0005 amu^{-1} can be regarded only as a typical minimum uncertainty.

Double spiking is a more powerful method for measuring, and correcting for, mass fractionation in TIMS Pb/Pb data, and it has been used for about 40 years. It has been conceptualized in several ways, leading to different computational methods to deal with the data, but these are all equivalent provided equivalent fractionation 'laws' have been assumed. Thirlwall [1] provides a contemporary assessment and historical review of these procedures.

The fundamental requirement for double spiking is to have a spike that is very different in isotopic composition to the samples being analysed, ideally with a high abundance of at least two isotopes that are minor components of the samples. Historically, most of the modelling for the process has been done with high-purity $^{207}Pb + ^{204}Pb$ spikes. There are other two-isotope alternatives, notably $^{202}Pb + ^{205}Pb$. Preparing and calibrating a double spike is a major commitment for any laboratory. High-purity spikes (>99%) are expensive, and they are not always available. This problem is somewhat alleviated by the high precision achievable with modern mass spectrometers, but there is a trade-off between spike purity and precision requirements. Regardless of the quality of the separated isotopes used to make it, calibrating any new multiple spike requires a substantial investment of laboratory resources.

The following discussion considers whether two widely distributed, readily available materials might be useful as double spikes, at least for a limited range of sample compositions.

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Specifically, I consider using the common-Pb standards SRM-981 and SRM-982 as spikes in conjunction with highly radiogenic Pb samples such as zircon and monazite.

2. Precision requirements

For geochronology based on highly radiogenic samples, the critical data ratio is ^{207}Pb/^{206}Pb. For samples of any Precambrian age, a fixed proportional error in ^{207}Pb/^{206}Pb translates to a relatively constant error in age. For example, a 0.1% error in ^{207}Pb/^{206}Pb corresponds with an age error of 2.0 Ma at ∼1000 Ma, reducing to 1.6 Ma at ∼3000 Ma. For most applications, uncertainties in ^{207}Pb/^{206}Pb dates are >2 Ma for reasons unrelated to mass fractionation of Pb, but precisions better than 5 Ma for individual analyses are common, so a total uncertainty of 0.1% in ^{207}Pb/^{206}Pb is a convenient benchmark.

The ^{207}Pb/^{206}Pb data vary directly with any applied correction for fractionation, so achieving a total uncertainty of 0.1% requires a fractionation correction to better than 0.1% (0.0010 amu^{-1}). Clearly, bias corrections cannot reliably achieve this. Data corrected by double-spiking with ^{204}Pb + ^{207}Pb or ^{202}Pb + ^{205}Pb spikes can be about an order of magnitude better.

3. Notation

The following text uses the abbreviations “Tr” (tracer) and “Unk” (unknown) for spike and sample, respectively (to avoid using the potentially ambiguous “S”), and “Mix” (mixture). The mixing ratio is $p = {}^{206}\mathrm{Pb}_{\mathrm{Tr}}/{}^{206}\mathrm{Pb}_{\mathrm{Unk}}$, which fits logically with the practice of adding spike to an aliquot of the sample solution immediately prior to filament loading. The only output parameter considered in f_{Unk}, the fractionation per amu in the sample data. In the figures, Δf_{Unk} is the error in f_{Unk} resulting from specified errors in the data for individual isotopes.

4. Modelling

4.1. Computation method

Computations follow the mixing-equation method of Gale [2], with ^{206}Pb as denominator isotope. The calculations assume linear fractionation. This might not be the most accurate model of fractionation but it is sufficient for the current exercise, which is concerned with the propagation of errors and uncertainties, not absolute accuracy.

Several scenarios have been considered, based on a range of zircon and monazite Pb isotopic compositions. In each case considered, the sample and spike isotopic compositions were selected, and the optimum p determined. Mixture compositions were generated for p varying across ∼3 orders of magnitude around the optimum, and the (fixed) Unk and (varying) Mix ratios fractionated by typical amounts. At each value of p, the synthetic data for each isotope was varied independently (i.e., an error was introduced to each numerator isotope abundance, as well as for the ^{206}Pb denominator, in turn), and the corresponding Δf_{Unk} determined.

Table 1
Rounded-off compositions used for spikes

	^{204}Pb/^{206}Pb	^{207}Pb/^{206}Pb	^{208}Pb/^{206}Pb
SRM-981	0.060	0.950	2.200
SRM-982	0.030	0.500	1.000

4.2. Assigning uncertainties

In order to consider the propagation of errors and uncertainties, it is necessary to assign values for these, for each of the data ratios. Each model scenario starts with an assigned precision of 0.005% for ^{207}Pb/^{206}Pb Unk data, and the errors applied to all the model data are defined by this precision limit. Modern mass spectrometers can give as good as 10 ppm (0.001%; 2 S.E.) for common-Pb samples or standards, so 0.005% is considered a reasonable estimate of the precision for small or low-^{207}Pb samples.

Assuming a counting-statistics relationship, the 0.005% is partitioned between ^{207}Pb and ^{206}Pb, then propagated from ^{206}Pb to the other isotopes for the Unk data. For the mixtures, the ^{206}Pb precision for Unk is propagated to ^{206}Pb in Mix assuming that there is a 2:1 split of the sample between the Unk and Mix aliquots, and that the recorded beam strengths correspond to this proportion. This gives the precision for the ^{206}Pb component of Mix, and from that the precision of the other isotopes in Mix.

This method of distributing measurement precision clearly takes no account of variations that an operator might make to maximise the precision of particular ratios, for example by varying integration times. It is seen below that the least precise isotope measurements are not necessarily those that contribute most to the final uncertainty in f_{Unk}.

4.3. Spike compositions

The compositions used for spikes (Table 1) are rounded-off values for SRM-981 and SRM-982. Although this modelling follows the algorithms and general logic of double spiking, the spikes are more correctly triple spikes, or perhaps quadruple spikes. However, this numeration is deceptive because the samples have only three abundant isotopes, unlike the four-isotope compositions normally considered in double-spiking of common Pb.

4.4. Sample compositions

Table 2 lists the sample compositions assessed. They have been chosen to cover a range of radiogenic mineral compositions, from low-Th zircon to monazite, with some range in ^{207}Pb/^{206}Pb. Two cases are included that were considered possible “weak-points” in the overall system, where parallel compositions might cause the computations to collapse or the propagated errors to expand unacceptably. One of these has ^{208}Pb/^{206}Pb for the sample equal to ^{208}Pb/^{206}Pb for the SRM-981 spike (possibly like some low-Th monazites), the other has ^{207}Pb/^{208}Pb equal.

Table 2
Sample compositions used in modelling

	^{204}Pb/^{206}Pb	^{207}Pb/^{206}Pb	^{208}Pb/^{206}Pb	Notes
Low-Th zircon	0.0001	0.0600	0.0200	Like CZ3
Typical zircon	0.0001	0.1000	0.3000	Proterozoic ^{207}Pb/^{206}Pb; "typical" Th/U
Old zircon	0.0001	0.3000	0.3000	Higher ^{207}Pb/^{206}Pb
Dangerous case 1 (high-Th zircon)	0.0001	0.1000	2.2000	^{208}Pb/^{206}Pb identical to SRM-981
Dangerous case 2	0.0001	0.1000	0.2316	^{207}Pb/^{208}Pb identical to SRM-981
Typical monazite	0.0001	0.1000	10.000	Higher Th/U than zircon

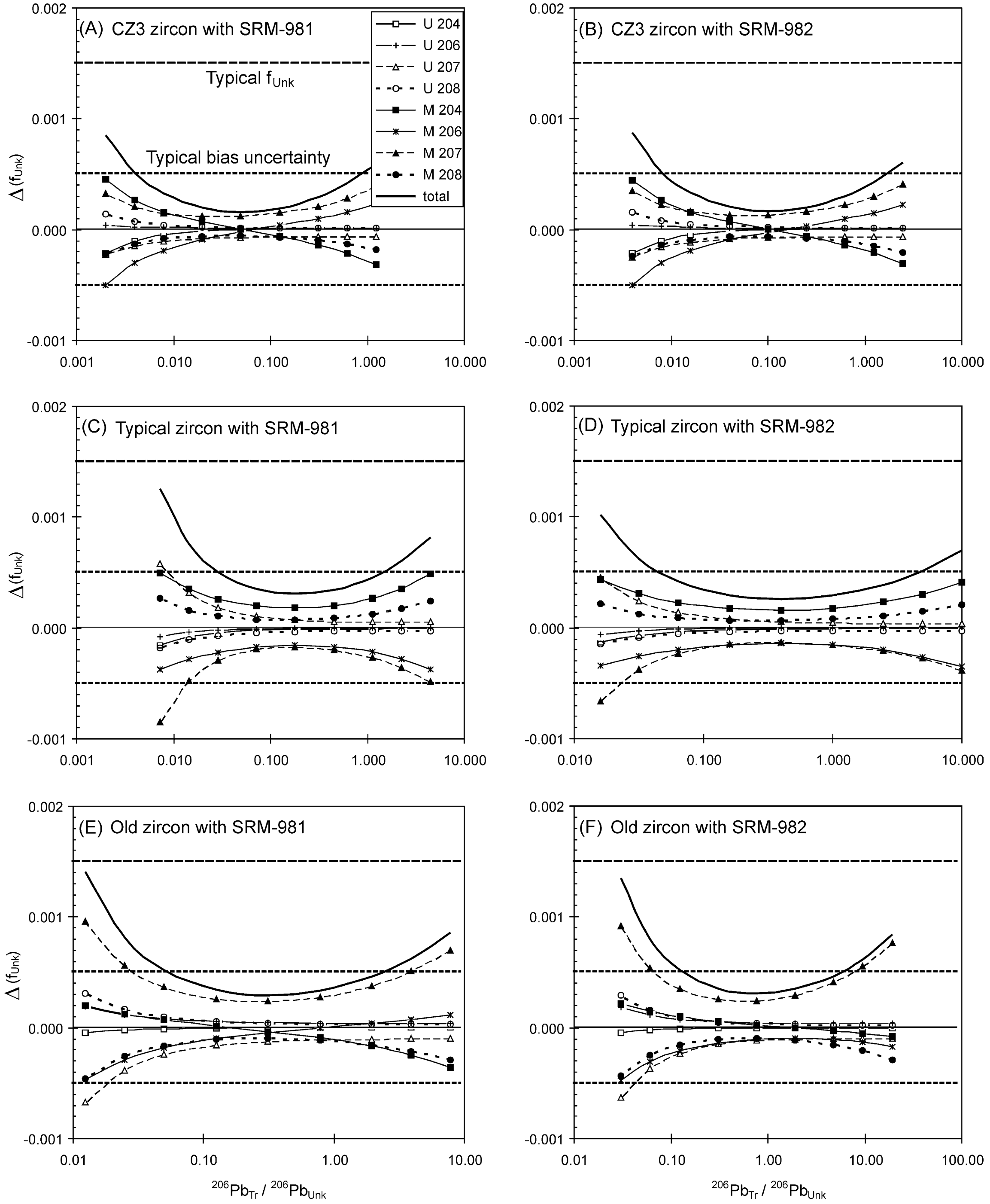

Fig. 1. Errors propagated to f_{Unk} from all data isotopes, across three orders of mixing ratio, for the spike and sample compositions in Tables 1 and 2. Coding of line symbols is given in [A], with U: Unk, M: Mix and Pb isotopes designated by their nominal mass. "Typical f_{Unk}" is the fractionation per amu typically observed in TIMS data using Faraday ion collectors; "Typical bias uncertainty" is a level of uncertainty commonly quoted for f_{Unk} in bias-corrected data.

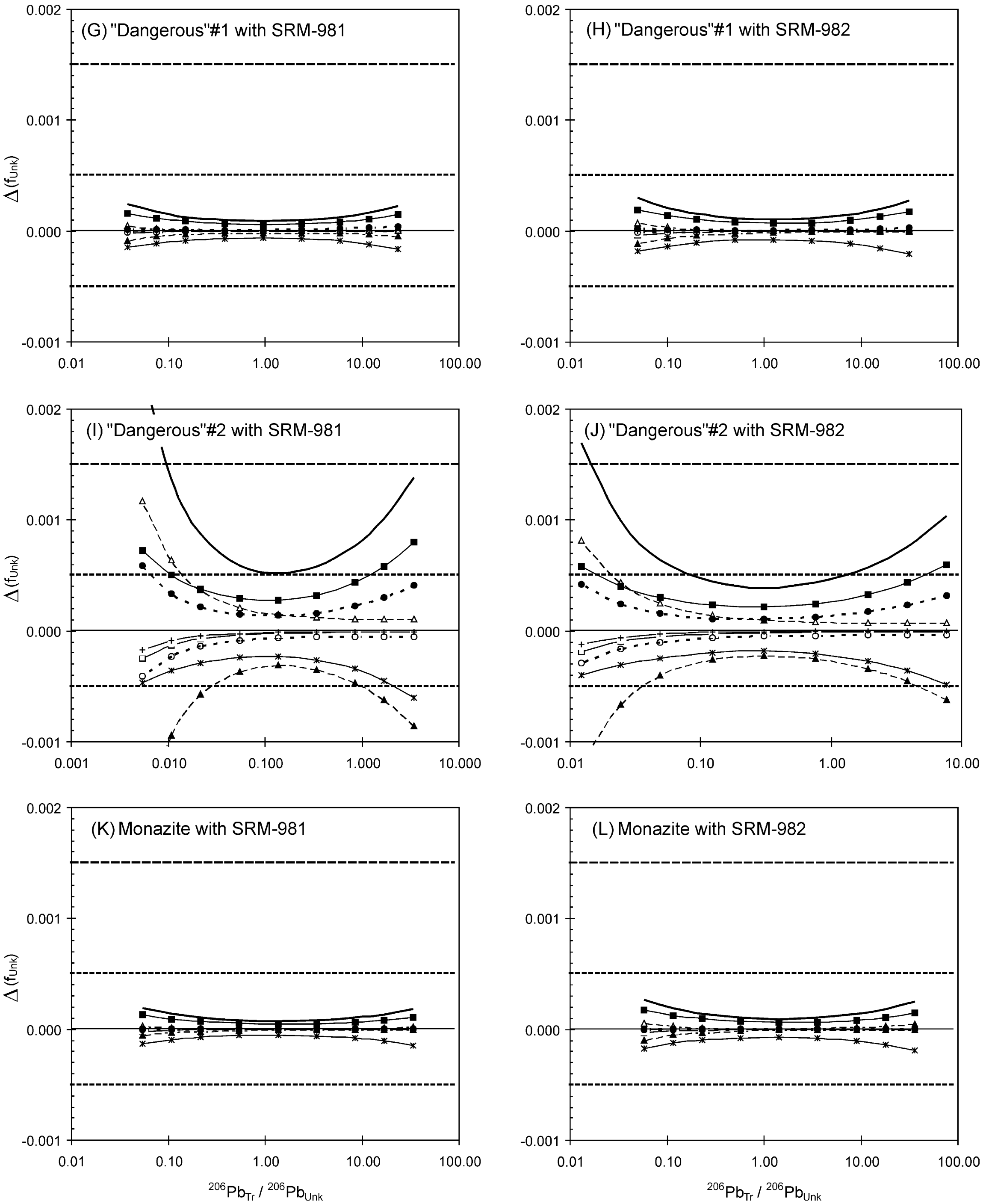

Fig. 1. (*Continued*).

5. Modelling results

The results are displayed in the Fig. 1A–L, each of which is labelled to identify the sample and spike compositions used. The various curves show the effect, at different mixing ratios p, of positive errors in each of the data isotopes (i.e., the isotope abundances in the synthetic data have been increased). In addition to the propagated error curves for individual isotopes, the plots include a "total" curve that is the total of the error curves, added in quadrature. All cases are plotted over about three orders of magnitude in p, but note that the optimum p varies appreciably, so the horizontal axis varies between plots. In all cases, the input error is the maximum of the range defined by the data precision (as in Section 4.2).

The overall impression from the plots is that, in each case, the collection of curves is roughly symmetric (using log[p]), with a span of at least one order in p where conditions are reasonably stable. However, the individual Δf_{Unk} curves show a range of forms, with some that are apparently asymptotic and some that cross through zero as p varies. In all cases except one of the anticipated problematic cases (Fig. 1I and J) the "total" curve lies below the typical 0.0005 uncertainty for bias corrections for more than an order of magnitude of p, and for several cases it approaches the levels expected for conventional double spiking for input data of the same precision.

Perhaps surprisingly, a major contributor to the uncertainty in f_{Unk} in some cases (e.g., Fig. 1A and K) is the precision of measurement of the abundant ^{206}Pb in Mix. In general, errors propagated to f_{Unk} from Mix are greater than those from Unk data, and in some cases (e.g., Fig. 1C and I) they dominate. These are obvious points for operator intervention, to modify integration times and improve data precision for that isotope. It may also be advantageous to make a 1:1 split of the sample for spiking, to improve the precision of the Mix data, at some cost to the precision of the Unk data. However, the optimum splitting and spiking conditions will need to be determined independently for any given sample composition.

6. Additional considerations

6.1. Aliquoting

In contrast to spikes that include two non-sample isotopes (notably ^{202}Pb + ^{205}Pb), but in common with ^{207}Pb + ^{204}Pb, using SRM-981 or SRM-982 requires splitting the Pb sample solution prior to mass spectrometric analysis. For very small samples, as in single-zircons analyses, this places extra demands on the instrumentation to maintain the precision of the Unk data. Furthermore, a complete sample analysis requires two Pb-isotopic analyses.

6.2. Other sources of fractionation

These procedures only control for mass fractionation that occurs after Tr is added to the Unk aliquot. They cannot determine fractionation that occurs during sample digestion or Pb separation.

6.3. Use two spikes?

Since aliquoting is required before spiking, these procedures cannot provide optimum Pb abundance data, especially for samples aliquoted from small sample volumes. Complete analyses for high-precision Pb/U data might therefore include spiking samples with a monoisotopic-Pb/U spike (using ^{202}Pb or ^{205}Pb) prior to sample digestion. Clearly this implies the calibration of the Pb/U spike, but there is still no need for a calibrated 2-isotope Pb component in that spike.

6.4. Sensitivity to blank

Using SRM-981 (and to a lesser extent, SRM-982) has the advantage that the data are essentially immune to corruption by common Pb blanks after the Unk aliquot has been separated and loaded. Any blank incorporated into Mix is likely to have an isotopic composition similar to Tr, so it has the effect of adding slightly more spike without making a significant change to the composition of the spike. For typical levels of blank, this has an insignificant effect on f_{Unk}. This does not alleviate any of the deleterious effects of blank acquired during sample digestion and separation, or in loading the Unk aliquot for analysis.

6.5. Absolute determination

Since SRM-981 and SRM-982 have well-determined, interlaboratory-referenced compositions, data that are fractionation-corrected by using them as double spikes are similarly intercomparable.

7. Conclusions

Using SRM-981 or SRM-982 as multiple spikes in conjunction with radiogenic Pb samples is a viable, readily accessible alternative to other means of correcting for mass fractionation in TIMS data. For most radiogenic mineral analyses it is more precise than bias corrections based on analyses of pure standards. However, it is not universally applicable, nor is it superior to established double-spiking procedures.

In the best cases (high-Th "monazite" sample compositions or very low-Th samples) the process works very well with either spike, with attainable precision approaching that for the established ^{204}Pb + ^{207}Pb or ^{202}Pb + ^{205}Pb spikes.

Even in the worst case considered (with identical ^{207}Pb/^{208}Pb in Unk and Tr), there is a narrow range of p where the precision of f_{Unk} would be comparable to the uncertainty in a bias correction. Although the outcome in such a case would not be appreciably more precise than from using a bias correction, it might be more reliable, and the uncertainty would be quantified. All other cases are better than this, with the "total" curve lying below 0.0005 for at least an order of magnitude range in p.

No cases were encountered that resisted computation.

There are minor, but possibly significant, differences consequent to choosing between SRM-981 and SRM-982.

Whether this procedure is useful in any laboratory would depend on the quality of raw data attainable. The data precision assumed for these models was intended to be conservative.

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References

[1] M.F. Thirlwall, Chem. Geol. 163 (2000) 299–322.
[2] N.H. Gale, Chem. Geol. 6 (1970) 305–310.