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Eliminating mass-fractionation effects on U-Pb isochron ages without double spiking

KENNETH R. LUDWIG*
Berkeley Geochronology Center, 2455 Ridge Road, Berkeley, CA 94709, USA

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Abstract—The utility of uranium-lead isochrons for dating rocks with a restricted range in U/Pb is limited by any uncertainty in the mass fractionation of the analysis. Double spiking (TIMS) or thallium normalization (ICP-MS) remove much of this limitation, as does the method of Getty and DePaolo (1995) for very young rocks. Optimal use of the 3-D "Total Pb/U isochron," however, is extremely simple to apply, requires only single-spiked TIMS analyses, and essentially eliminates fractionation-related age imprecision for rocks of any age. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

Unlike Rb-Sr or Sm-Nd systems, the daughter element of the U-Pb isotope system has no pair of isotopes whose ratio is invariant. As a result, the accuracy of isotopic ratio measurements via TIMS (thermal ionization mass spectrometry) is generally limited by a mass-fractionation uncertainty of 0.03 to 0.08% per mass unit[1] for analyses of Pb. Such mass-fractionation effects can be largely eliminated with double (or triple) spiking (e.g., Dodson, 1970; Woodhead and Hergt, 1997; Todt et al., 1996; Galer, 1999; Thirlwall, 2000), at the cost of additional analytical effort and extra care (because of the sensitivity of geochemical and geochronological studies to ^{207}Pb and ^{204}Pb cross-contamination). Alternatively, analysis via multicollector, sector ICP-MS with normalization to a natural thallium spike (Walder and Furuta, 1993; Belshaw et al., 1998; Halliday and Rehkämper, 1998; White et al., 2000) will also reduce mass-fractionation error. I wish to show here, however, that the most straightforward way to eliminate mass-fractionation effects on U-Pb isochron ages is simply to use appropriate input data for the "Total Pb/U isochron" (Ludwig, 1998).

2. QUATERNARY U-PB ISOCHRONS

In their innovative paper on U-Pb dating of very young rocks, Getty and DePaolo (1995) pointed out that because the buildup of radiogenic ^{207}Pb in very young rocks or minerals is extremely small, ^{207}Pb/^{204}Pb will be essentially invariant with time. The Pb isotopic analyses of cogenetic systems of this age can therefore be normalized to the measured ^{207}Pb/^{204}Pb for one of the analyses, permitting very high sample-to-sample precision (but not accuracy) in the ^{207}Pb/^{206}Pb measurements and acceptable precision when the age is calculated from a ^{238}U/^{207}Pb –^{206}Pb/^{207}Pb or ^{238}U/^{204}Pb –^{206}Pb/^{204}Pb regression. Any bias in the ^{206}Pb/^{207}Pb measurements (from use of a relative, rather than absolute, mass-fractionation correction) is immensely demagnified in the age calculation, so that even the very modest radiogenic increment of ^{206}Pb in Quaternary samples can yield isochron ages with precisions at the percent level or better, provided that the requirement of a single common Pb with precise isotopic homogeneity is maintained.

The mathematics of extracting a U-Pb age from a ^{238}U/^{207}Pb–^{206}Pb/^{207}Pb regression appear complex (Getty and DePaolo, 1995; Rasbury et al., 1997) but can be made accessible in visual terms. First (as discussed in Ludwig, 1998), it should be recognized that the ^{238}U/^{207}Pb –^{206}Pb/^{207}Pb parameters of the method are essentially those of the Tatsumoto U-Pb concordia diagram (Tatsumoto et al., 1972), which is in turn a minor mathematical transformation of the familiar Tera-Wasserburg concordia diagram (Tera and Wasserburg, 1972), wherein $x = {}^{238}\text{U}/{}^{206}\text{Pb}$ and $y = {}^{207}\text{Pb}/{}^{206}\text{Pb}$. On the Tera-Wasserburg concordia diagram for total (as opposed to radiogenic) Pb, the ^{238}U/^{206}Pb –^{207}Pb/^{206}Pb regression is seen to be a mixing line between the system's initial Pb (which plots on the y-axis) and the system's radiogenic Pb (which plots on the U-Pb concordia curve at a point corresponding to its age). Therefore, the age solution for the isochron is the lower concordia-intercept age for the regression line, and the usual algorithms for determining concordia-intercept ages and errors (e.g., Ludwig, 1980, 2000) can be used.

3. USING THE TOTAL PB/U ISOCHRON WITH HIGH-PRECISION ISOTOPIC MEASUREMENTS

The Total Pb/U isochron, as defined in Ludwig (1998) and implemented in Ludwig (1999), is the concordia-constrained, 3-D linear regression of U-Pb isotope data on any of the 3-D U-Pb concordia diagrams (Neymark and Levchenkov, 1979; Wendt, 1984; Zheng, 1990); for example, the 3-D Tera-Wasserburg concordia ($x = {}^{238}\text{U}/{}^{206}\text{Pb}$, $y = {}^{207}\text{Pb}/{}^{206}\text{Pb}$, $z = {}^{204}\text{Pb}/{}^{206}\text{Pb}$). The defining characteristic of the Total Pb/U isochron is that on any of the 3-D concordia diagrams, the intercept of the regression line with the ^{204}Pb-free plane is constrained to fall somewhere on the U-Pb concordia curve. As for any U–Pb isochron, the Total Pb/U isochron requires a single, isotopically homogeneous initial Pb, a single age for all of the samples on the isochron, and a closed system history. The advantages of this isochron over any of the other Pb/U (or Pb-Pb) isochrons are optimum precision (because of the inclusion of all of the relevant Pb-isotopic information, not just a subset), a quantitative test of U-Pb age-concordance, and recovery of both the ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb initial ratios (together with their errors and error correlation).

The ability of the Total Pb/U isochron to eliminate the precision-degrading effects of Pb mass-fractionation on the isochron age was not mentioned in the original paper (Ludwig,

* (kludwig@bgc.org).
[1] All errors in this paper are 2σ.

1998). However, it is an inherent feature of this isochron that with correct assignment of the errors and error correlations of the input data, the usual imprecision in TIMS Pb-isotopic measurements that arise from variable mass fractionation has no effect on the resulting isochron age. As a result, dramatic improvements in age precision are possible for samples of any age.

3.1. Details

Though not strictly essential, to maximize the within-run precision of the Pb isotopic analyses, it is advisable to normalize the measured Pb-isotopic ratios for within-run drift of mass-fractionation. This normalization must be done independently for each analysis (for example, to the first block of measured data), using any of the Pb isotope ratios as the normalizing ratio. For isotopic compositions anywhere near that of typical common Pb, the optimum ratio for normalization (in terms of the most precise corrections for mass fractionation) will be $^{206}Pb/^{208}Pb$. If the ^{208}Pb ion beam is too intense for measurement, the $^{206}Pb/^{207}Pb$ will be the most efficient (the normalizing ratio need not be the same for each sample). With modern multicollector TIMS instruments and in the absence of any isobaric interferences, the within-run precision of the resulting Pb isotopic ratios should be no worse than a few tens of ppm, provided that ion beams for ^{206}Pb and ^{207}Pb can be maintained at more than $\sim 10^{-11}$ amperes (and for ^{204}Pb at $>4 \times 10^{-13}$ amperes), requiring perhaps 20 to 40 ng of more-or-less common Pb.

When setting up the data table for the Total U/Pb isochron (the 3-D Tera Wasserburg concordia diagram will be used for discussion), the run-to-run mass-fractionation error in the Pb-isotope measurements must be included, despite the high within-run precision of the Pb-isotope measurements. If (1) the ^{206}Pb ion beam is $>10^{-11}$ amperes on a multicollector mass spectrometer, (2) the $^{206}Pb/^{204}Pb$ is reasonably nonradiogenic (say <30, so that ^{204}Pb measurement error remains small), and (3) neither isobaric interferences nor correction for Pb blank are significant, then the mass-fractionation error will typically lead to $^{207}Pb/^{206}Pb$ –$^{204}Pb/^{206}Pb$ error correlations of perhaps -0.999 (see Appendix for equations and derivation). These error correlations cannot be satisfactorily approximated by blanket or "typical" values; for the purposes of the Total Pb/U isochron, an error correlation of -0.9995 is much different from one of -0.995.

The error correlations of $^{238}U/^{206}Pb$ with $^{207}Pb/^{206}Pb$ and $^{204}Pb/^{206}Pb$ will be essentially zero if a separate spiked analysis is used for the Pb concentration determinations. However, if a single ^{205}Pb-spiked analysis is used, significant *x-y* and *x-z* error correlations can arise, because the mass fractionation affects the $^{206}Pb/^{205}Pb$ ratio along with the $^{207}Pb/^{206}Pb$ and $^{204}Pb/^{206}Pb$ ratios (see Appendix for equations).

The mathematics of the Total Pb/U isochron offer no obvious hints as to how mass-fractionation effects are eliminated from the isochron age, although it is intuitively clear that this result arises from the additional information provided by the addition of a third isotope ratio combined with the constraint of the U-Pb concordance of the intercept on the *x-y* plane. A graphical visualization may help, however (Fig. 1). For the types of isochrons we are most concerned with—those with little dispersion in $^{204}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$–almost all of the spread of the data will be in the x-direction. With *x-y* and *x-z* error correlations of zero (i.e., a separate spiked-Pb analysis), the error ellipsoids of the data will appear as collinear, pancake-like discoids pierced by and dispersed along the Total Pb/U isochron line and tilted along a plane perpendicular to the shortest chord to the x-axis. Because the error ellipsoids are very highly flattened and nearly coplanar, the statistically permissible isochron lines (that is, the ones that pierce the error ellipsoids) sweep along the near-plane defined by the ellipsoids at an oblique angle to the concordia curve in the *x-y* plane. This geometry greatly restricts the statistically acceptable locus on the concordia curve intersected by the isochron so that, despite a limited dispersion along the isochron, the precision of the isochron age remains acceptably high.

4. AN ALTERNATE (BUT INELEGANT) METHOD

Although the Total Pb/U Isochron is the most straightforward and precise algorithmic approach to eliminating mass-fractionation effects from U-Pb isochron ages, at least one other approach can be used. This method, a logical extension of the Getty and DePaolo (1995) approach and perhaps best characterized as a "bootstrap isochron," can be summarized as follows:

1. Calculate an approximate age using, for example, the lower concordia-intercept on a Tera-Wasserburg concordia diagram (or by a geologic guess, if stratigraphic restrictions are more reliable).
2. Calculate a best-estimate initial $^{207}Pb/^{204}Pb$ using a $^{235}Pb/^{204}Pb$–$^{207}Pb/^{204}Pb$ isochron (or, if more reliable, estimate from isotope-geochemical considerations).
3. Calculate the predicted $^{207}Pb/^{204}Pb$ for each of the samples using the age from step 1, the initial $^{207}Pb/^{204}Pb$ from step 2, and the measured $^{235}U/^{204}Pb$ ratios, for example,

$$\left(\frac{^{207}Pb}{^{204}Pb}\right)_{predicted} = \left(\frac{^{207}Pb}{^{204}Pb}\right)_{initial} + \left(\frac{^{235}U}{^{204}Pb}\right)(e^{\lambda_{235}t} - 1)$$

4. Calculate the estimated mass fractionation from the ratio of the predicted $^{207}Pb/^{204}Pb$ to the measured $^{207}Pb/^{204}Pb$, for example,

$$f = \sqrt[3]{\frac{(^{207}Pb/^{204}Pb)_{predicted}}{(^{207}Pb/^{204}Pb)_{measured}}}$$

5. Corrected the measured $^{207}Pb/^{206}Pb$ for mass fractionation using the result from step 4, for example,

$$(^{207}Pb/^{206}Pb)_{corrected} = f \times (^{207}Pb/^{206}Pb)_{measured}$$

6. Calculate a corrected age from the lower intercept on the Tera-Wasserburg concordia diagram, using the measured $^{238}U/^{206}Pb$ and corrected $^{207}Pb/^{206}Pb$ from step 5. Use the within-run $^{207}Pb/^{206}Pb$ errors (i.e., without including a mass-fractionation error) and a $^{238}U/^{206}Pb$ –$^{207}Pb/^{206}Pb$ error correlation of zero.
7. Iterate steps 3 to 6 to convergence.

Because of its reliance on a single, relatively low-precision isotope ratio ($^{207}Pb/^{204}Pb$), the age from this "bootstrap isochron" will be somewhat less precise than from the Total Pb/U Isochron (because it makes less efficient use of the available information), and the age-error calculated from the final regression will be somewhat of an underestimate. Nonetheless, a large improvement in age precision (compared with conventional U-Pb isochrons using single-spiked TIMS data) is obtained as a result of the effective normalization of Pb mass-fractionation.

5. BLANK CORRECTIONS AND ^{204}PB ERROR

The greatest advantage of the Total Pb/U isochron is realized with high-precision measurements, which require a very small

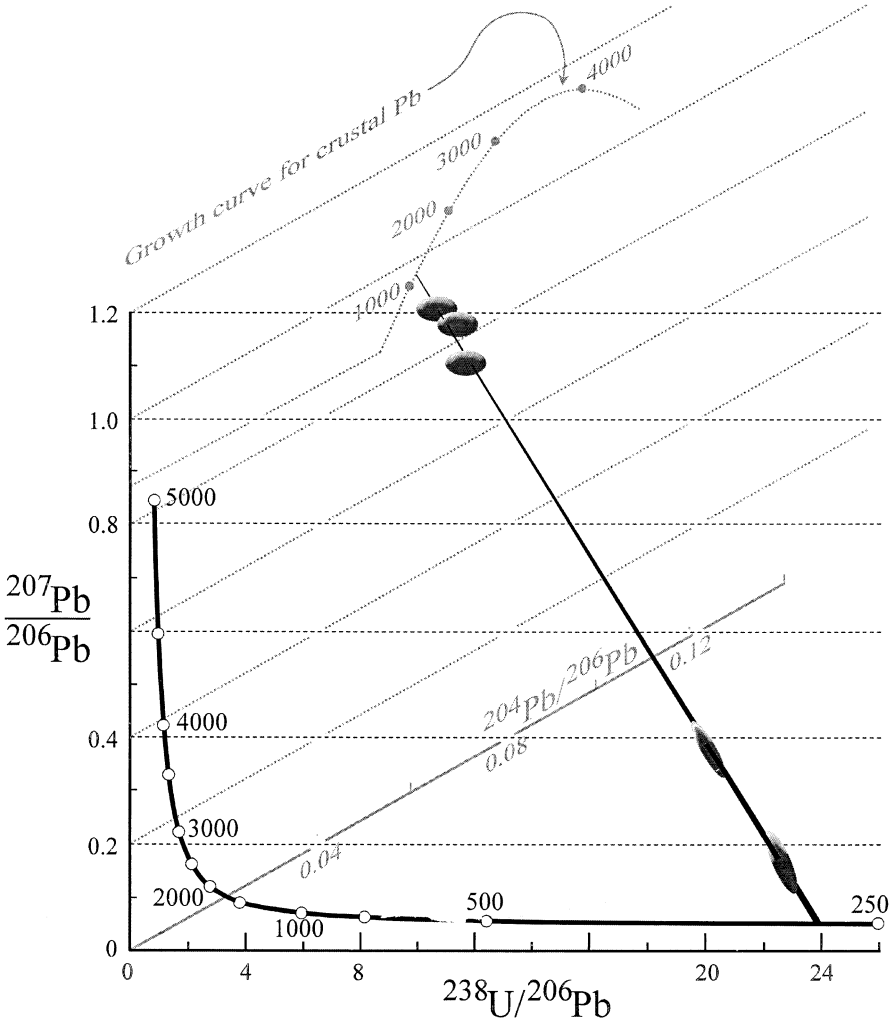

Fig. 1. Graphical representation of a Total Pb/U. Shaded ellipsoids represent error ellipsoids of data points (not to scale). For the type of data discussed in this article, the actual ellipsoids would plot either as thin, pancake-like ellipsoids oriented normal to the shortest chord to the x-axis (Pb concentrations determined from a separate, spiked analysis) or as spindle-shaped ellipsoids oriented normal to a chord to the origin and tilted along a plane joining the y-axis (Pb concentrations and compositions determined from a single, ^{205}Pb-spiked analysis).

correction on the Pb-isotope ratios from laboratory contamination (blank). As long as the radiogenic component of the sample Pb is small (which is the case of most interest here), a Sample-Pb:Blank-Pb ratio of more than 500 to 1000 will be acceptable, resulting in less than 0.01% additional error on the blank-corrected ^{206}Pb/^{204}Pb ratio. For more radiogenic Pb-isotope ratios (e.g., ^{206}Pb/^{204}Pb > 100), the blank correction will exceed 0.1%. Moreover, as the ^{204}Pb ion beam drops below 10^{-13} amperes, the ^{204}Pb measurement error will grow dramatically, so that, in the absence of ^{205}Pb-spiking as described in a later section, there will be little advantage in the Total Pb/Isochron. In such cases, however, the ^{238}U/^{206}Pb uncertainty will be the major limitation on isochron-age precision rather than ^{206}Pb/^{204}Pb and ^{207}Pb/^{206}Pb uncertainty (see Section 9), so that provided the other Pb and U isotopes are precisely measured, errors arising from both blank and ^{204}Pb measurement should remain a subordinate consideration.

6. ISOBARIC INTERFERENCES

Some studies using a double spike to correct for Pb mass discrimination with TIMS have observed that the true (run-to-run) precision attainable is distinctly worse than within-run precision (perhaps because of unidentified isobaric interferences in the Pb mass spectrum, e.g., Thirlwall, 2000), with some workers suggesting a true 2σ precision for double-spiked Pb-isotope ratios of no better than 0.02% (e.g., Fölling et al., 2000). Thus attainment of true TIMS fractionation-corrected precisions of 20 to 50 ppm for Pb-isotopic ratios (as permitted by amplifier noise and counting-statistics limits) may await solution of such problems and is no less limiting for the Total Pb/U isochron approach than for double-spiked conventional isochrons.

7. ACCURACY OF MASS-FRACTIONATION ESTIMATES

Because the average mass fractionation when running actual samples (being more-or-less impure because of imperfect

Table 1. Mesozoic age (180 Ma) with small spread in $^{206}Pb/^{204}Pb$.

$^{238}U/^{204}Pb$	$^{206}Pb/^{204}/Pb$	$^{207}Pb/^{204}Pb$	$^{238}U/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{204}Pb/^{206}Pb$
10	18.749	15.520	0.5323	0.82784	0.05334
25	19.188	15.561	1.3015	0.81099	0.05212
45	19.758	15.593	2.2765	0.78924	0.05061
83	20.805	15.616	3.9824	0.75062	0.04807
130	22.180	15.732	5.8597	0.70928	0.04509

Range of true $^{206}Pb/^{204}Pb$ = 18%.
Total-Pb/U isochron = 179.93 ± 0.18 [±0.30] Ma.
$^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$ isochron* = 179.1 ± 1.0 [±1.1] Ma.

*Equivalent to the lower concordia intercept on the uncorrected (total Pb) Tera-Wasserburg concordia diagram. Precisions of the corresponding $^{238}U/^{204}Pb-^{206}Pb/^{204}Pb$ isochrons will be somewhat worse to nearly the same, depending on the dispersion of the data points.

chemical purification) can be significantly different than the value inferred from replicate runs of pure standards, not only can the mass-fractionation correction for TIMS Pb analyses be unreliable, but also the estimate of random uncertainty in this correction (e.g., Woodhead et al., 1995). Fortunately, simulations demonstrate that with the Total Pb/U Isochron, such biases in the mass-fractionation estimate do not significantly effect either the accuracy of the isochron age or its calculated error (see examples below).

8. EXAMPLES

In the examples described in this section, synthetic input data have been generated in the following way:

1. The true mass fractionation differs (on average) from the assumed fractionation by +0.1%/amu (to demonstrate insensitivity to such a bias), with a run-to-run variation of 0.08%/amu (rather worse than generally assumed).
2. The $^{238}U/^{206}Pb$ error is specified to be 0.15% (easily obtainable using a $^{233}U + ^{236}U$ or $^{233}U + ^{235}U$ double spike, or with care using a ^{235}U single spike), uncorrelated with the $^{207}Pb/^{206}Pb$ and $^{204}Pb/^{206}Pb$ ratios (the case for separate spiked and unspiked Pb-analyses).
3. The within-run errors are specified at two levels (Low/High) For $^{207}Pb/^{206}Pb$, errors are 0.003%/0.02%, and for $^{204}Pb/^{206}Pb$ errors are 0.005%/0.02%. With the mass-fractionation error taken into account, these values yield Low/High run-to-run errors of 0.08006%/0.08246% for $^{207}Pb/^{206}Pb$ and 0.1601%/0.16125% for $^{204}Pb/^{206}Pb$, with an error correlation of −0.99881/−0.96265 (see Appendix for details);
4. U/Pb values (as $^{238}U/^{204}Pb$), initial $^{207}Pb/^{206}Pb$ and $^{204}Pb/^{206}Pb$, and true ages are specified arbitrarily.
5. The true isotope ratios are calculated to fit precisely on the Total Pb/U isochron for the specified age, and the synthetic measured ratios are perturbed a random (Gaussian) amount with a variance consistent with the errors and error correlations specified in step 3.
6. Total Pb/U isochron ages and errors are calculated using Isoplot/Ex (Ludwig, 1999).
7. Age errors are given for both Low and High input errors, with the latter in square brackets.
8. See examples in Tables 1–4.

As these examples show, for *x*, *y* and *x z* error correlations near zero (e.g., separate spiked and unspiked analyses), the smaller the dispersion in $^{206}Pb/^{204}Pb$ (or $^{207}Pb/^{206}Pb$), the greater the precision advantage of the Total Pb/U isochron. For sufficiently large isotope-ratio dispersions (e.g., Table 4), the mass fractionation error in $^{207}Pb/^{206}Pb$ is a negligible part of the age

Table 2. Early Tertiary age (50 Ma) with extremely small spread in $^{206}Pb/^{204}Pb$.

$^{238}U/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{238}U/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{204}Pb/^{206}Pb$
1.00	18.473	15.506	0.0540	0.83941	0.05413
2.18	18.491	15.518	0.1178	0.83923	0.05408
3.25	18.481	15.496	0.1758	0.83846	0.05411
5.40	18.500	15.500	0.2915	0.83780	0.05405
7.21	18.510	15.495	0.3887	0.83710	0.05402

Range of true $^{206}Pb/^{204}Pb$ = 0.26%.
Total-Pb/U isochron = 50.28 ± 0.63 [±3.6] Ma.
$^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$ isochron* = 58 ± 20 [±20] Ma.

*Equivalent to the lower concordia intercept on the uncorrected (total Pb) Tera-Wasserburg concordia diagram. Precisions of the corresponding $^{238}U/^{204}Pb-^{206}Pb/^{204}Pb$ isochrons will be somewhat worse to nearly the same, depending on the dispersion of the data points.

Table 3. Mid-Quaternary age (0.5 Ma) with minute spread in true $^{206}Pb/^{204}Pb$.

$^{238}U/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{238}U/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{204}Pb/^{206}Pb$
10	18.4780	15.5213	0.5398	0.83999	0.054118
21	18.4597	15.4969	1.1348	0.83950	0.054172
37	18.4600	15.4959	2.0019	0.83943	0.054171
59	18.4645	15.4998	3.1914	0.83943	0.054158
77	18.4691	15.5034	4.1580	0.83942	0.054144

Range of true $^{206}Pb/^{204}Pb$ = 0.028%.
Total-Pb/U isochron = 0.521 ± 0.058 [±0.33] Ma.
$^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$ isochron* = 1.0 ± 1.8 [±1.9] Ma.
Getty-DePaolo method† = 0.532 ± 0.078 [±0.48] Ma.

*Equivalent to the lower concordia intercept on the uncorrected (total Pb) Tera-Wasserburg concordia diagram. Precisions of the corresponding $^{238}U/^{204}Pb-^{206}Pb/^{204}Pb$ isochrons will be somewhat worse to nearly the same, depending on the dispersion of the data points.

†Getty and DePaolo, 1995. For Quaternary samples, simulations indicate that the Getty-DePaolo procedure approaches (but never quite equals) the precision of the properly applied Total Pb/U isochron.

Table 4. Early Paleozoic age (450 Ma) with large spread in $^{206}Pb/^{204}Pb$.

$^{238}U/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{238}U/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{204}Pb/^{206}Pb$
300	40.163	16.747	7.466	0.41697	0.024899
687	68.052	18.281	10.070	0.26863	0.014695
1200	105.141	20.369	11.395	0.19373	0.009511
1750	144.847	22.587	12.065	0.15593	0.006904
2492	198.122	25.522	12.536	0.12882	0.005047

Range of true $^{206}Pb/^{204}Pb$ = 6x.
Total-Pb/U isochron = 450.27 ± 0.46 [±0.46] Ma.
$^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$ isochron* = 450.35 ± 0.47 [±0.47] Ma.

*Equivalent to the lower concordia intercept on the uncorrected (total Pb) Tera-Wasserburg concordia diagram. Precisions of the corresponding $^{238}U/^{204}Pb-^{206}Pb/^{204}Pb$ isochrons will be somewhat worse to nearly the same, depending on the dispersion of the data points.

error, which instead becomes limited by the $^{238}U/^{206}Pb$ errors. This will be true for the effect of a blank correction as well (given an adequate $^{204}Pb_{blank}/^{204}Pb_{sample}$ ratio of >1000), even for the relatively radiogenic compositions of Table 4.

9. EXPLOITING HIGH PRECISION, ^{205}PB-SPIKED ANALYSES WITH THE TOTAL PB/U ISOCHRON

If a uranium double-spike (e.g., $^{233}U + ^{236}U$ or $^{233}U + ^{235}U$) is used for uranium-concentration determination, and the ion beams for both the spike isotopes and ^{238}U are maintained at $>10^{-12}$ amperes, the precision of the uranium-concentration determinations can be better than 0.01%, as can the within-run precision of the $^{206}Pb/^{205}Pb$ measurement given similar ion-beam intensities. If only one, ^{205}Pb-spiked Pb-isotopic analysis is used (as opposed to separate aliquots for Pb concentration and isotopic composition), the dominant error term for not only the Pb isotope measurements, but also for the $^{238}U/^{206}Pb$ measurement, will then be the Pb mass-fractionation uncertainty of, for example, ~0.05%. As a result, if the within-run precisions of the other Pb isotope ratios are sufficiently precise, the errors in the corrected $^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$-$^{204}Pb/^{206}Pb$ measurements will become highly correlated—in the range of about −0.96 to −0.99 and +0.96 to +0.99, respectively (see Appendix for details). Instead of the flattened, pancake-like error ellipsoids formed by data points with zero *x, y* and *x, z*error correlations, the error ellipsoids for these data points will contract to a spindle shape (highly stretched, prolate spheroids) oriented normal to a chord to the *x, y, z* origin at all loci along the isochron.

For samples with very small increments of radiogenic ^{206}Pb (e.g., Tables 2 and 3), high *x, y* and *x, z* error correlations will have little effect on the precision of the resulting Total Pb/U isochron age and can even be ignored. But for larger degrees of radiogenic ^{206}Pb buildup (e.g., Table 4), such high *x, y* and *x, z* error correlations can greatly improve the precision of the isochron age. This effect can be understood graphically (Fig. 2) by examining the effect of a high *x,y* error correlation on the Concordia age[2] of a concordant, purely radiogenic data point. The effect on the Total Pb/U isochron age with low-^{204}Pb data points is analogous because the resulting age arises from projecting the isochron to the concordia curve through a point that lies slightly "behind" the *x,y* plane. As Figure 2 demonstrates, the age precision of the analysis with uncorrelated errors is limited by the mass-fractionation imprecision on the $^{206}Pb/^{205}Pb$ ratio used to calculate the $^{238}U/^{206}Pb$ ratio and so is ~0.08%. The age precision of the analysis with correlated errors, however, is more than 4 times better (~0.02%), a result of the "thinning" of the *x, y* error ellipse when the correlated error is considered.[3]

The advantage of ^{205}Pb-spiking diminishes in rough proportion to the ^{204}Pb content of the most-radiogenic point. For instance, if the data of Table 4 were measured with a U-concentration precision of 0.01% and a within-run $^{206}Pb/^{205}Pb$ precision of 0.005%, the isochron-age error using a separate ^{205}Pb-spiked analysis ($\rho_{x,y} = \rho_{x,z} = 0$, where ρ indicates error correlation) would be 0.25 Ma. With a single ^{205}Pb-spiked analysis ($\rho_{x,y} = -0.9897$, $\rho_{x,z} = +0.9899$), the isochron age error would decrease by a relatively modest factor of two. Whether this potential for age precisions well under the permil level is more than a statistical curiosity remains to be seen, given that

- It is difficult enough to obtain very small samples of minerals capable of yielding reproducible ages at the permil level. To obtain much larger samples that have behaved as a closed system to an order of magnitude tighter tolerance seems unlikely.
- Improvement of age precision is minimal (<2×) for samples between 1200 and 3600 Ma, where the Concordia curve is subparallel to the error ellipse and the advantage of an oblique intersection of a narrow error ellipse with the concordia curve is lost.
- The accuracy of any U/Pb or Pb-Pb age is limited by the uncertainties of the ^{238}U and ^{235}U decay constants (0.11% and 0.16%, respectively; Jaffey et al., 1971).

10. CAVEATS ON THE BENEFITS OF THE TOTAL PB/U ISOCHRON

A limitation of the Total Pb/U isochron for single-spiked TIMS data, compared with an isochron with true mass-fractionation correction, is that no improvement in the precision of the calculated initial-Pb isotope ratios is realized: these ratios (the intercept on the *y-z* plane) will still be limited by fractionation imprecision and bias. Another is that, because the true isotope ratios of each sample are limited by mass-fractionation imprecision (although the age precision is not), should excess scatter be encountered with an isochron having little dispersion in $^{207}Pb/^{206}Pb$, one cannot effectively explore approaches such as a planar 3-D U-Pb regression (e.g., Neymark and Levchenkov, 1979; Wendt, 1984; Zheng, 1990), which can deal with complications such as episodic disturbance or an initial Pb that is dispersed along a secondary isochron.

A third and perhaps the most important limitation is one shared by double-spiked and thallium-normalized ICP-MS isochrons. Any U-Pb isotope data set that could benefit significantly from precise correction for mass fractionation would be vulnerable to even small amounts of random isotopic variation in the common-Pb end member of the isochron. If this variation is completely uncorrelated with the U/Pb ratio of the samples, the effect will simply be an increase of scatter about the isochron, and thus an elevated MSWD. Simulations indicate that the usual error expansion (of the final age) of the 2σ a priori errors of the total Pb/U isochron age by $\sqrt{\text{MSWD}} \times t$ is adequate to account for such an increased uncertainty. (t is Student's t for the $2N-3$ degrees of freedom of the Total Pb/U isochron.)

But if the total range in $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{206}Pb$ is very small, the increase in scatter arising from even very small variations in the initial Pb-isotope ratios can be disastrous to the precision of the resulting isochron age. For instance, consider the 0.5 Ma isochron of Table 3 with "Low" errors: the precision

[2] The analog of the Total Pb/U isochron for purely radiogenic Pb (Ludwig, 1998).

[3] Note that even though the blank-corrected precision of the $^{206}Pb/^{204}Pb$ ratio can be very poor for high measured $^{206}Pb/^{204}Pb$, provided that the precision of the measured $^{206}Pb/^{205}Pb$ and $^{207}Pb/^{206}Pb$ remains high, the precision-enhancing effects of the high $^{238}U/^{206}Pb_{radiogenic}$–$(^{207}Pb/^{206}Pb)_{radiogenic}$ error-correlation will be maintained.

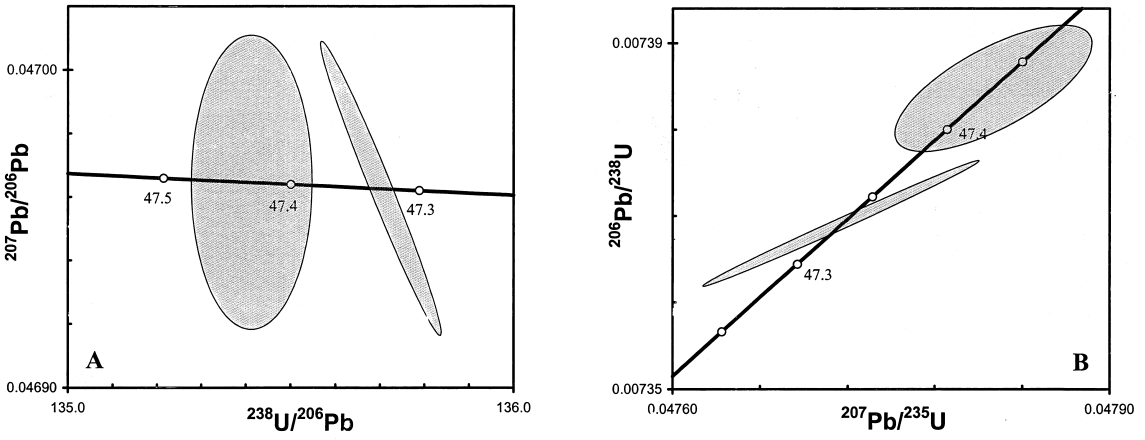

Fig. 2. Effect of error correlation on the precision of a Total Pb/U isochron age for highly radiogenic data (or, equivalently, for a Concordia age) of a precise ^{205}Pb-spiked U-Pb analysis, shown on both Tera-Wasserburg concordia (A) and conventional concordia (B) diagrams. Error ellipse at left (A) and top (B) is for uncorrelated errors (e.g., separate analyses for Pb isotopic composition and concentration) and is dominated by the assigned 0.08%/amu mass-fractionation error (0.01% within-run precision assumed for Pb-isotope ratios and [U]). Error ellipse on right (A) and bottom (B) is for a single, ^{205}Pb-spiked Pb analysis with the same mass-fractionation error, but taking into account the error correlation resulting from the shared effect of mass fractionation on the $^{206}Pb/^{205}Pb$ and $^{207}Pb/^{206}Pb$ ratios.

of the Total Pb/U isochron age in the absence of "geologic" (that is, nonanalytical) scatter is 0.058 Ma. However, including a random scatter of, for example, 0.003 in the initial $^{206}Pb/^{204}Pb$, together with a scatter of 0.00034 in initial $^{207}Pb/^{204}Pb$ (i.e., a very small amount of an ~1850 Ma radiogenic-Pb component) increases the age error to 0.27 Ma—a significant degradation. The effect of such a component on the Getty-DePaolo method is even larger, with the age error increasing to 0.52 Ma. The point here is that a 0.003 variation in the initial $^{206}Pb/^{204}Pb$ is extremely small and may be impossible to avoid for rocks formed in crust with a sufficiently ancient ancestry. Moreover, if this isotopic variation in initial Pb is more or less correlated with the U/Pb ratio of the sample, a significant bias in the age can result.

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APPENDIX

Expressions. for Errors and Error Correlations

Define *X, Y, Z* as the measured $^{238}U/^{206}Pb$, $^{207}Pb/^{206}Pb$, and $^{204}Pb/^{206}Pb$, respectively; *x, y, z* as the corresponding fractionation-corrected ratios; and ε as the run-to-run variation in mass fractionation, expressed as the fractional bias per mass-unit difference of the isotopes (so if the mass fractionation were +0.05%/amu with an uncertainty of 0.03%/amu, then $\varepsilon = 0.0005$ and $\sigma_\varepsilon = 0.0003$). Assuming a power law for mass fractionation (linear or exponential laws give the same result),

$$y = (1 + \varepsilon)Y \tag{1}$$

and

$$z = \frac{Z}{(1+\varepsilon)^2} \tag{2}$$

so that

$$\frac{dy}{y} = \frac{dY}{Y} + \frac{d\varepsilon}{1+\varepsilon} \tag{3}$$

$$\frac{dz}{z} = \frac{dZ}{Z} - 2\frac{d\varepsilon}{(1+\varepsilon)^2} \tag{4}$$

which, because the covariances of *Y*, ε and *Z*, ε are zero, and ε is small, gives

$$\left(\frac{\sigma_y}{y}\right)^2 = \left(\frac{\sigma_Y}{Y}\right)^2 + \sigma_\varepsilon^2 \tag{5}$$

$$\left(\frac{\sigma_z}{z}\right)^2 = \left(\frac{\sigma_Z}{Z}\right)^2 + 4\sigma_\varepsilon^2 \tag{6}$$

.

Although the Tera-Wasserburg concordia is often chosen because of a supposed freedom from significant error correlations, for high-precision analyses the *y, z* errors must be very highly anticorrelated, given that the effect of mass fractionation is to shift the *Y* and *Z* in opposite directions. The covariances are obtained by multiplying the differentials, giving (treating the *Y*, ε and *Z*, ε covariances as before)

$$\frac{\mathrm{cov}(y,z)}{yz} \cong \frac{\mathrm{cov}(Y,Z)}{YZ} - 2\sigma_\varepsilon^2 \tag{7}$$

.

The covariance on the right of the equation, although never precisely zero (because the ^{206}Pb measurement is the denominator in both *Y* and *Z*), can be neglected because of the dominance of the ^{204}Pb measurement error (typically 5 or more times greater than the ^{206}Pb error). The *y, z* error correlation $\rho_{y,z}$ is then written as

$$\rho_{y,z} \equiv \frac{\mathrm{cov}(y,z)}{\sigma_y\sigma_z} = -\frac{2\sigma_\varepsilon^2}{(\sigma_y/y)(\sigma_z/z)} \tag{8}$$

.

Should the Pb-isotope data be available only as $^{206}Pb/^{204}Pb$-$^{207}Pb/^{204}Pb$ (= *u*-*v*, for example) rather than $^{207}Pb/^{206}Pb$-$^{204}Pb/^{206}Pb$ (= *y*-*z*, for example), the following transformation equations can be used:

$$\left(\frac{\sigma_u}{u}\right)^2 = \left(\frac{\sigma_z}{z}\right)^2 \tag{9}$$

,

$$\left(\frac{\sigma_y}{y}\right)^2 = \left(\frac{\sigma_u}{u}\right)^2 + \left(\frac{\sigma_v}{v}\right)^2 - 2\left(\frac{\sigma_u}{u}\right)\left(\frac{\sigma_v}{v}\right)\rho_{uv} \tag{10}$$

, and

$$\rho_{yz} = \frac{(\sigma_u/u) - (\sigma_v/v)\rho_{uv}}{(\sigma_y/y)} \tag{11}$$

.

If the Pb concentration is determined by a separate spiked analysis, the *x,y* and *x,z* error correlations will be zero. If, however, a single, ^{205}Pb-spiked analysis is used (for both Pb concentration and Pb isotopic composition), significant *x, y* and *x, z* error correlations can exist. Thus, defining *U* as the ^{238}U concentration, *W* as the measured $^{206}Pb/^{205}Pb$ ratio, and *s* as concentration of ^{205}Pb in the (for simplicity, isotopically pure) spike,

$$x = \frac{U}{Ws(1+\varepsilon)} \tag{12}$$

$$\frac{dx}{x} = \frac{dU}{U} - \frac{dW}{W} - d\varepsilon \tag{13}$$

$$\left(\frac{\sigma_x}{x}\right)^2 \cong \left(\frac{\sigma_U}{U}\right)^2 + \left(\frac{\sigma_W}{W}\right)^2 + \sigma_\varepsilon^2 \tag{14}$$

$$\frac{\mathrm{cov}(x,y)}{x,y} \cong -\sigma_\varepsilon^2 \tag{15}$$

$$\frac{\mathrm{cov}(x,z)}{x,z} \cong -2\sigma_\varepsilon^2 \tag{16}$$

so

$$\rho_{x,y} = -\frac{\sigma_\varepsilon^2}{(\sigma_x/x)(\sigma_y/y)} \tag{17}$$

$$\rho_{x,z} = +\frac{2\sigma_\varepsilon^2}{(\sigma_x/X)(\sigma_z/z)}. \tag{18}$$