Modeling apparent Pb loss in zircon U-Pb geochronology

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Abstract. ~~Although~~ Because the loss of radiogenic Pb from zircon is known to be a major factor that can cause inaccuracy in the U-Pb geochronological system, there is a need to better characterize the distribution of Pb loss in natural samples ~~has not been well characterized~~. Treatment of zircon by chemical abrasion (CA) has become standard practice in isotope dilution-thermal ionization mass spectrometry (ID-TIMS), but CA is much less commonly employed prior to *in-situ* analysis via laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) or secondary ionization mass spectrometry (SIMS). Differentiating the effects of low levels of Pb loss in Phanerozoic zircon with relatively low precision *in-situ* U-Pb dates, where the degree of Pb loss is insufficient to cause discernible discordance, is challenging. We show that U-Pb isotopic ratios~~dates~~ that have been perturbed by Pb loss may be modeled by convolving a Gaussian distribution that represents random variations from the true isotopic value stemming from analytical uncertainty ~~the unperturbed U-Pb date distribution,~~ with a distribution that characterizes Pb loss. We apply this mathematical framework to model the distribution of apparent Pb loss in 10 igneous samples that have both non-CA LA-ICP-MS or SIMS U-Pb dates and an estimate of the crystallization age, either through CA U-Pb or $^{40}Ar/^{39}Ar$ geochronology. All but one sample showed negative age offsets that were unlikely to have been drawn from an unperturbed U-Pb date distribution. Modeling apparent Pb loss using the logit-normal distribution produced good fits with all 10 samples and showed ~~Because Pb loss is constrained to values between -100% and 0%, we suggest that the logit-normal distribution may be an appropriate~~ ~~.~~ ~~Although the distribution type(s) that characterize Pb loss are not well known, we show that the logit-normal distribution~~ ~~Of the eight continuous distribution types we considered, modeling apparent Pb loss using the Weibull distribution produced, on average, the closest match with the non-CA U-Pb date distributions. We show~~ two contrasting patterns in apparent Pb loss: samples where most zircon U-Pb dates undergo a bulk shift and samples where most zircon U-Pb dates exhibited low age offset but fewer ~~grains~~ dates had more significant offset. Our modeling framework allows comparison of relative degrees of apparent Pb loss between samples of different age, with the first and second Wasserstein distances providing useful estimates of the total magnitude of apparent Pb loss. Given that the large majority of *in-situ* U-Pb dates are acquired without the CA treatment, this study highlights a pressing need for improved characterization of apparent Pb loss distributions in natural samples to aid in interpreting non-CA *in-situ* U-Pb data and to guide future data collection strategies.

1 Introduction

Zircon U-Pb geochronology is arguably one of the most important radiometric dating approaches used by geoscientists, with widespread application to constraining the age of Pleistocene and older geologic materials (Davis et al., 2003; Schoene, 2013; Gehrels, 2014). We rely on zircon U-Pb dates for calibrating the geological time scale (e.g., Compston, 2000a; 2000b; Bowring and Schmitz, 2003; Gradstein et al., 2004; Kaufmann, 2006), constraining the timing of important Earth history events (Froude et al., 1983; Schoene et al., 2010~~; 2015~~; Burgess et al., 2014), and determining the rates of Earth processes (Rioux et al., 2012; Schoene et al., 2012; Johnstone et al., 2019~~; Schoene et al., 2019~~). The zircon U-Pb geochronometer is particularly powerful due to the ability to assess agreement between the $^{238}U \rightarrow ^{206}Pb$ and $^{235}U \rightarrow ^{207}Pb$ decay chains, with $^{206}Pb^{*}/^{238}U$ and $^{207}Pb^{*}/^{235}U$ dates in agreement plotting on the Concordia line, where * indicates radiogenic Pb (Wetherill, 1956).~~ For example, a zircon that has undergone loss of radiogenic Pb will be pulled off the Concordia line towards the origin, thus becoming discordant (Fig. 1).~~

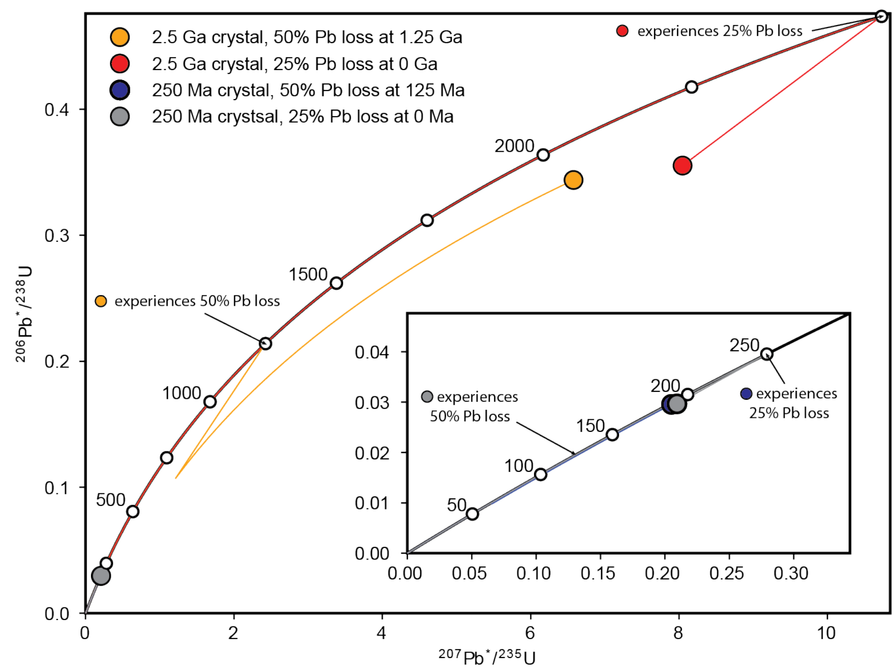

Figure 1. Illustration of the influence of Pb loss on 250 Ma and 2.5 Ga zircon. Two Pb loss scenarios are shown: 25% loss at half the age of the zircon and 50% loss at present-day (0 Ma). The approximately linear nature of the $^{206}Pb^{*}/^{238}U$ vs $^{207}Pb^{*}/^{235}U$ Concordia line near the origin results in Pb loss producing limited discordance if the Pb loss occurs within several 100s of Myr of crystallization. Note that a greater amount of ancient Pb loss is required to produce the same shift in $^{206}Pb^{*}/^{238}U$ relative to recent Pb loss. Thin, colored lines represent the path of each zircon.

The causes and complications of open system behavior (e.g., radiogenic Pb loss) in zircon have long been a topic of ~~concern~~ study (Tilton et al., 1955; Pidgeon et al., 1966). Although Pb loss events may be discerned on U-Pb Concordia diagrams in some circumstances and can provide useful geologic information about the thermal and/or fluid flow history of a region (Silver and Deutsch, 1963; Blackburn et al., 2011; Morris et al., 2015; Kirkland et al., 2017), ~~with~~ recognizing ~~and mitigating the effects of~~ Pb loss ~~remaining~~ remains a ~~major~~ challenge when it occurs within several 100's Myr of crystallization (Fig. 1; Anderson et al., 2019). ~~.~~ For example, due to the shape of the ^{206}Pb*/^{238}U versus ^{207}Pb*/^{235}U Concordia line, Pb loss in Phanerozoic zircon ~~that occurs within several 100's Myr after crystallization~~ results in ~~discordance developing at a very low angle relative to the Concordia line. This~~a 'sliding along concordia' effect that can make Pb loss difficult to discern, particularly in relatively low-precision *in-situ* (i.e., LA-ICP-MS or SIMS) datasets when the Pb loss ~~only~~ produces concordant or only modestly ~~discordance~~ discordant analyses (e.g., <10%; Ashwal et al., 1999; Bowring and Schmitz, 2003; Ireland and Williams, 2003; Reimink et al., 2016; Spencer et al., 2016; Watts et al., 2016; Anderson et al., 2019). Such low levels of Pb loss have been termed 'cryptic' and may be associated with spatial heterogeneities including radiation-damaged U-rich zones and microstructures (Nasdala et al., 2005; Kryza et al., 2012; Watts et al., 2016). Most Pb loss in zircon is likely a consequence of recrystallization or Pb transport in crystals with severe radiation damage and exposure to hydrothermal alteration (Silver and Deutsch, 1963; Pidgeon et al., 1966; Mezger and Krogstad, 1997; Cherniak and Watson, 2001; ~~Mezger and Krogstad, 2004;~~ Marsellos and Garver, 2010). Mechanisms for Pb loss may include metamorphism (~~Kroner~~ Kröner et al., 1994; Orejana et al., 2015; Zeh et al., 2016), hydrothermal alteration (Geisler et al., 2002, 2003); diagenetic fluids or fluid flow (Willner et al., 2003; Morris et al., 2015; Kirkland et al., 2020), and chemical weathering (Stern et al., 1966; Black, 1987; Balan et al., 2001; Pidgeon et al., 2017; Andersen and Elburg, 2022). Pb loss is thought to primarily occur at temperatures <250°C in which radiation damage in zircon is unable to be annealed over geologic timescales (Schoene, 2013).

Zircon domains that have lost Pb may be preferentially removed by first thermally annealing the zircon at high temperature (e.g., 800-1100°C) and then partially dissolving the zircon in a heated HF solution in a technique called chemical abrasion (CA) (Mattinson, 2005). The CA treatment is now routinely applied in ID-TIMS analysis and has contributed to both improved precision and accuracy of CA-ID-TIMS U-Pb data (Schoene, 2013). Although some *in-situ* U-Pb laboratories practice thermal annealing routinely (e.g., Allen and Campbell, 2012; Solari et al., 2015), CA has been applied much less frequently (Crowley et al., 2014; von Quadt et al., 2014; Watts et al., 2016; Ver Hoeve et al., 2018; Ruiz et al., 2022). Several studies that have conducted paired analysis of non-CA and CA of the same samples via *in-situ* U-Pb geochronology have found the non-CA U-Pb dates to skew younger than the CA U-Pb dates (Crowley et al., 2014; von Quadt et al., 2014; Watts et al., 2016). A growing number of maximum depositional age studies with tandem non-CA LA-ICP-MS and CA-ID-TIMS dating have shown the youngest non-CA U-Pb dates tend to be younger than expected~~to skew young~~ relative to CA U-Pb dates or other geologic constraints, even when considering measurement uncertainty (e.g., Herriott et al., 2019; Schwartz et al., 2022; Howard et al., 2022; Sharman et al., 2023). However, there is a lack of quantitative constraints on the relative importance of Pb loss in influencing non-CA U-Pb date distributions acquired via *in-situ* mass spectrometry, particularly as related to influencing depositional age constraints (Copeland, 2020).

This study builds upon past research on open system behavior in zircon by ~~presents~~ presenting a ~~novel~~ mathematical framework for ~~quantifying the effects~~characterizing the distribution of apparent Pb loss on untreated (i.e., non-CA) U-Pb date distributions. We first suggest that U-Pb isotopic ratios that have been ~~loss~~ perturbed by Pb loss ~~U-Pb date distributions, or age offsets,~~ may be viewed as the convolution of two signals: a Gaussian distribution that reflects measurement uncertainty about the true isotopic ratio ~~the unperturbed U-Pb date distribution~~ and the distribution that characterizes Pb loss. We then apply this mathematical framework to model the distribution of apparent Pb loss that has affected 10 igneous samples of Miocene to Carboniferous age. ~~-~~Our results highlight the importance of quantifying distributions of apparent Pb loss magnitude ~~-~~to better understand the potential influence on non-CA zircon U-Pb date distributions.~~s, with a need for improved characterization of~~ ~~to better resolve both the distribution types and magnitudes associated with Pb loss in zircon.~~

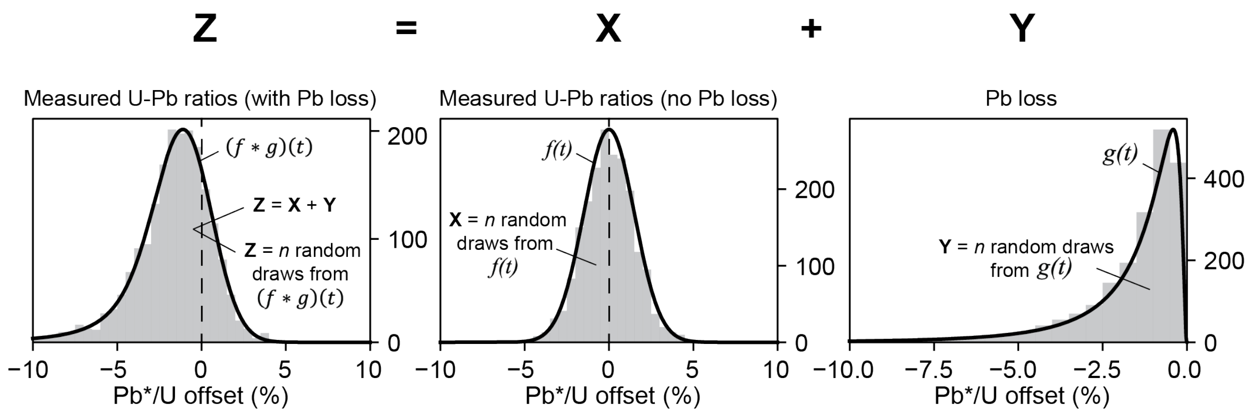

Figure 2. Illustration of how Pb*/U isotopic ratios from *n* zircon analyses that have been perturbed by Pb loss (Z) may be modeled as the summation of *n* non-perturbed Pb*/U ratios (X) and the amount of Pb loss encountered by each (Y). X is drawn from *f(t)* that reflects the Gaussian distribution of Pb*/U ratios that are unperturbed by Pb loss and Y is drawn from *g(t)* that represents the distribution of Pb loss in the sample. The distribution that characterizes Z may be found by convolving *f(t)* and *g(t)*. Although we assume that *f(t)* is a Gaussian distribution, the distribution type of Pb loss, *g(t)*, shown in this example as a logit-normal distribution (μ=-4.5, σ=1.0) could take a number of discrete or continuous forms (Fig. 3). Note that in our modeling framework, values of X, Y, and Z are normalized as percentage deviation from the true isotopic ratio (i.e., the mean of *f(t)*), where negative values indicate that measured Pb*/U is lower than the true ratio. See Supplemental Video 1 for an animation that illustrates the process of convolution and Supplemental Video 2 for an exploration of the logit-normal distribution in μ and σ parameter space.

2 Mathematical framework

A series of *n* ~~measurements of Pb loss-perturbed U-~~Pb*/U measurements that have undergone Pb loss~~dates~~, **Z**, may be modeled as the sum of the corresponding unperturbed Pb*/U~~U-Pb~~ values~~dates~~, **X**, and the amount ~~of~~ that Pb*/U changed due to~~Pb loss encountered by each date~~ Pb loss for each date, **Y**,

$$Z = X + Y \qquad \text{(Equation 1)}$$

where **Z**, **X**, and **Y** are all 1-D matrices with *n* values and units of percentage offset from the true isotopic value (Fig. 2~~1~~). Because Pb loss produces a lower Pb*/U~~U-Pb~~ ratio~~date~~, the values of **Y** must be negative in our formulation of Equation 1 ~~(Fig. 1)~~. If **X** ~~We assume that **X**~~ is drawn from a Gaussian distribution *f(t)* whose mean (μ) approximates the true isotopic value and whose standard deviation (σ) reflects dispersion from the true value related to measurement uncertainty (e.g., Schoene et al., 2013) and if **Y** is drawn from a distribution that reflects Pb loss, *g(t)*, ~~. the U-Pb measurements unperturbed by Pb loss (X) have a shared true isotopic value, μ, and that the unperturbed U-Pb ratiosdates (**X**) from cogenetic zircon may be characterized by a Gaussian distribution, *f(t)*, whose mean (μ) equals the crystallization age and standard deviation (σ) reflects the degree to which the values of **X** deviate from the shared crystallization age. If these U-Pb ratios are then subjected to Pb loss (**Y**) that is drawn from *g(t)*, and if **X** and **Y** are independent,~~ then **Z** may be viewed as being drawn from the convolution of *f(t)* and *g(t)*

$$(f * g)(t) = \int_{-\infty}^{\infty} f(\tau) g(t - \tau) d\tau \qquad \text{(Equation 2)}$$

provided that **X** and **Y** are independent ~~where *g(t)* is reflected about the y-axis and shifted in τ space~~ (Fig. 2~~1~~; Supplemental Video 1). Convolution simply represents the summation of two random variables, in this case one related to analytical precision (i.e., random variation around the true isotopic value stemming from the measurement process) and the other related to the geologic process of Pb loss. We model Pb loss as percentage offset from the true Pb*/U ~~isotopic ratio~~ ~~vaue~~ value ~~crystallization age~~ rather than deviation in absolute time (i.e., Myr) to promote comparison of samples of different age (Fig. 2~~1~~).

~~Because Pb loss is always negative and at most -100% of the crystallization age, we constrain *g(t)* is constrained to values between 0% and -100%.~~

$$\cancel{g(t) = \{0\%\ if\ g(t) > 0\%\ g(t)\ if -100\% \le g(t) \le 0\% -100\%\ if\ g(t) \le -100\%}$$

Equation 2 may be solved analytically for some forms of *f(t)* and *g(t)*. For example, the convolution of Gaussian and exponential distributions is known as the exponentially modified Gaussian distribution (Grushka, 1972~~; Fig. 1; Supplemental Video 1~~). However, $(f * g)(t)$ may also be solved numerically, which has the advantage of allowing both *f(t)* and *g(t)* to take any form.

~~Because Pb loss is always negative and at most -100% of the crystallization age, g(t) is constrained to values between 0% and -100%. A sample where all zircon crystals undergo the same amount of Pb loss~~

~~Figure 32 illustrates the effects of boththree discrete and continuous forms of *g(t)* on normally distributed U-Pb isotopic ratiosdates drawn from *f(t)*. A sample that experienced no Pb loss can be thought of as the convolution of *f(t)* with a discrete form of *g(t)* where the 100% of probability corresponds to 0% Pb loss (Fig. 32a).~~

~~Having 100% of probability for a discrete amount of Pb loss that is >0% produces a bulk shift in the U-Pb age distribution (i.e., constant Pb loss; Fig. 32b). Similarly, Pb loss experienced by only a subset of grains, or isolated Pb loss, may also be modeled using a discrete distribution, (Fig. 32c). Alternatively, the Pb loss function *g(t)* could be represented by a continuous probability distribution, where values of Pb loss vary continuously between values of 0% and -100% (Fig. 3d3). Figure 3 illustrates the effects of eight different types of continuous distributions on modifying a Gaussian distribution following convolution.~~

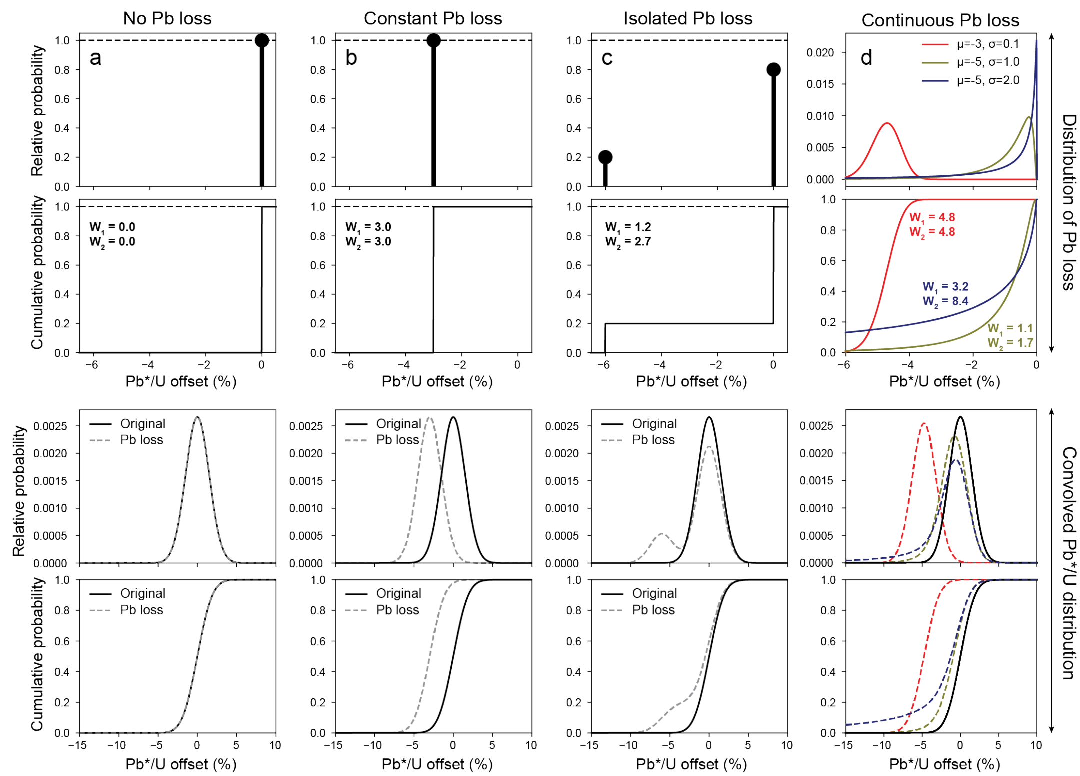

Figure 3. Illustration of how normally distributed zircon Pb*/U values may be perturbed by discrete (a-c) or continuous (d) distributions of Pb loss. The top row represents the distribution of Pb loss in the sample expressed as a percentage of the true isotopic ratio (e.g., ^{206}Pb*/^{238}U or ^{207}Pb*/^{235}U) at the time of Pb loss, where the height of the black bar and ball indicates the relative probability of the specified Pb*/U offset. Three discrete scenarios are shown: a) no Pb loss, b) constant Pb loss, and c) isolated Pb loss. A logit-normal distribution is shown as an example of continuous Pb loss in d). Additional examples of continuous Pb loss distributions are shown in Figure A1. The bottom row shows both the relative (above) and cumulative (below) probabilities of the unperturbed (solid black line) and Pb loss-perturbed (dashed line) Pb*/U distributions.

3 Methods

3.1 Modeling approach

We use the mathematical framework described above to model both the distribution of apparent Pb loss, *g(t)*, experienced by a group of cogenetic ~~grains~~ crystals and their unperturbed U-Pb date distribution, *f(t)*. ~~Because *g(t)* could represent any geological or analytical process that introduces negative age offsets, we use the phrase "apparent Pb loss" when describing our modeled estimates of *g(t)*. For instance, matrix-related systematic errors (Allen and Campbell, 2012), addition of U-Th during weathering (Pigdeon et al., 2019), and even sample contamination from younger minerals could introduce negative age shifts exclusive of loss of radiogenic Pb. It should also be noted that the distribution of "apparent Pb loss" will underestimate the magnitude of the true Pb loss event in the case of ancient Pb loss. This point is illustrated in Fig. 1 where a 50% reduction in Pb* at 125 Myr after crystallization produces a similar offset in 206Pb*/238U versus the same grain that lost 25% of its Pb* at 250 Myr (present day). If~~ Because Pb loss is isotopically indiscriminate, Equation 2 may be equally applied to ^{206}Pb*/^{238}U and ^{207}Pb*/^{235}U. However, we model ^{206}Pb*/^{238}U ratios as these have much lower analytical uncertainty for the Carboniferous and younger samples analyzed in this study.

To model *g(t)*, we allow the μ of *f(t)* to vary within the 95% confidence interval associated with an independent estimate of the crystallization age. We then estimate both *g(t)* and σ of *f(t)* by iteratively solving for the combination of parameters that minimize the misfit between the measured Pb*/U ~~-Pb dates~~values and the modeled distribution $(f * g)(t)$ using the Python scipy.optimize.minimize() function. We define misfit as the sum of squared residuals between the empirical cumulative distribution function (ECDF) of the measured ~~U-Pb dates~~Pb*/U values and the cumulative density function (CDF) of the modeled ~~U-Pb age~~ Pb*/U distribution. ~~In total, we consider 11 different distribution types for *g(t)* that consist of both discrete (no Pb loss, constant Pb loss, and isolated Pb loss; Fig. 2) and continuous (uniform, gamma, exponential, Rayleigh, Weibull, Pareto, half-normal, and lognormal; Fig. 3) distributions.~~

If both non-CA and CA analyses are available from the same sample, then the distribution of CA U-Pb dates may be used to constrain the parameters of *f(t)*. For such samples, we modify the approach described above by first finding the Gaussian distribution *f(t)* that most closely approximates the treated ~~U-Pb date~~Pb*/U distribution. We then use this best-fitting *f(t)* in estimating *g(t)* using the minimization-of-misfit technique described above. Such datasets have the advantage of providing constraints on σ of *f(t)*, which is otherwise treated as an unknown parameter during modeling if only non-CA U-Pb dates are available.

In order to estimate *g(t)* as described above, we must choose one or more reasonable parametric models that are appropriate for describing distributions of Pb loss. One possibility is that all zircon crystals in the sample experienced the same amount of Pb loss, which could shift Pb*/U from 0% to -100% of its value~~ because Pb loss is always negative and at most -100%~~. Such a scenario of constant Pb loss may be modeled by a discrete form of *g(t)* where a single parameter specifies the percentage of Pb lost~~ (<0% and >-100%)~~. Convolution of such a discrete form of *g(t)* simply produces a negative shift in the ~~U-Pb~~Pb*/U values (i.e., Fig. 3b).

Another possibility is that Pb loss was experienced by only a subset of ~~grains~~crystals (i.e., isolated Pb loss). This scenario may also be modeled by assigning *g(t)* to a discrete distribution with two parameters: one that indicates the fraction of Pb lost ~~(<0% and >-100%)~~ and one that specifies the proportion of ~~grains~~crystals that underwent Pb loss (Fig. 3c). This parameterization of *g(t)* will produce a bimodal pattern in U-Pb values, particularly if the degree of Pb loss is significant relative to measurement uncertainty (Fig. 3c).

Instead of modeling *g(t)* as a discrete distribution where Pb loss is restricted to certain values, we may also consider a continuous probability distribution where values of Pb loss can take on any value between 0% and -100% (Fig. 3d). ~~Because~~Rather than assume ~~we do not know~~ *a priori* the form(s) that *g(t)* might take, we considered a wide range of 1- or 2-parameter distributions for the purposes of exploratory modeling (Appendix A). Of the distribution types considered, we identified the logit-normal distribution, also known as the logistic normal distribution, as perhaps the most reasonable for modeling Pb loss. The logit-normal distribution has the property of having a logit (i.e., the quantile function of the logistic distribution) that is normally distributed with a geometric mean of μ and standard deviation of σ (Aitchison and Shen, 1980; Mead, 19654)~~.~~

$$f(x,\mu,\sigma) = \frac{1}{\sigma\sqrt{2\pi}}\frac{1}{x(1-x)}e^{-\frac{(logit(x)-\mu)^2}{2\sigma^2}} \qquad \text{(Equation 3)}$$

for $0<x<1$.

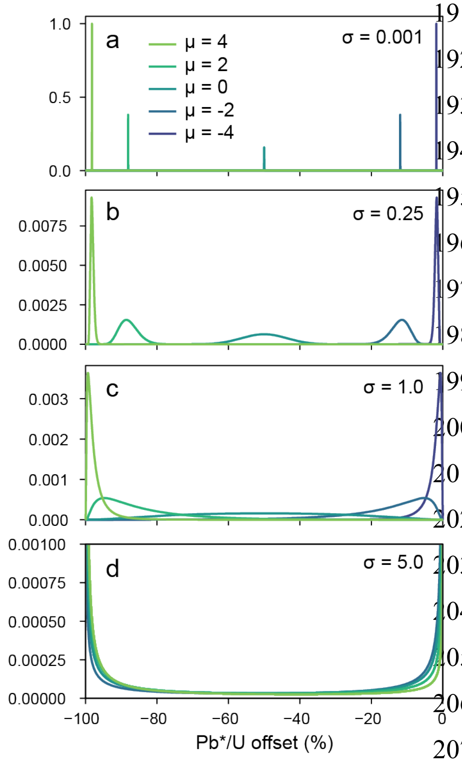

Figure 4. Exploration of the logit-normal distribution's parameter space. Note that we have rescaled the x-axis of the logit-normal distribution such that $-100<x<0$.

The logit-normal distribution is well-suited for modeling constrained data types (e.g., compositional data; Atchison and Bacon-Shone, 1999; Vermeesch, 2018b) in part due to it being defined over $0<x<1$. We invert and scale the distribution to extend from $-100\%<x<0\%$ to match the sign and units of Pb*/U offset due to Pb loss when expressed as a percentage (Fig. 3d).

Figure 4 explores the relationship of the logit-normal distribution to its two parameters (μ and σ) (see also Supplemental Video 2). The distribution has a 'spikey' character when σ is a very small number (e.g., 0.001; Fig. 4a), which would be a reasonable approximation for samples that underwent an approximately constant amount of Pb loss (e.g., Figs. 3a and 3b). Although the logit-normal distribution cannot model 0% or 100% Pb loss, these values may be approximated by making μ a large negative or positive number, respectively. A sample where most zircon exhibit very little Pb loss but with fewer zircon experiencing significant Pb loss could be produced by μ = -4 and σ = 1.0 (Fig. 4c). Alternatively, a sample with a peak probability of ~~Pb loss~~Pb*/U offset $<0\%$ may be modeled using moderate values of σ (e.g., 0.25-1; Figs. 4b and 4c). The logit-normal distribution produces bimodal distributions where most probability is close to 0% and -100% when σ values are high (e.g., $>>1$; Fig. 4d).

3.2 Samples

We apply the mathematical and modeling framework presented above to estimate the distribution of apparent Pb loss in 10 igneous samples that range in age from Carboniferous to Miocene, nine of which have been published previously (Table 1). Samples CTU, RCP, and SRF are all from upper Eocene rhyolites of the Caetano caldera system of the western United States (Watts et al., 2016). These samples were split into non-CA and CA aliquots prior to analysis via SIMS (Watts et al., 2016). We used the error-weighted mean age of the CA U-Pb dates as an estimate of the true crystallization age for each sample, with weighted means approximately 0.4-0.6 Myr older than the corresponding $^{40}Ar/^{39}Ar$ sanidine ages (Watts et al., 2016). The number of analyses per aliquot (non-CA or CA) ranges from 17-34 for these three samples (Table 1).

Table 1. Sample Summary

					Model results (best fit logit-normal distribution)					
Sample	Age (Ma)	Reference	N (non-CA)	N (CA)	*f(t)* (Ma)	*g(t)* sum of squared residuals	*g(t)* parameters	*g(t)* P2.5-P50-P97.5 (%)	W_1	W_2
ELM18 DVTC-10	15.7 ± 0.2 (2σ)[1]	Miller et al. (2022)	144	n.a.	15.90 ± 0.55 (1σ)	1.0	μ = -3.24 σ = 1.28	-32.49 -3.77 -0.32	6.9	11.1
248-2	24.422 ± 0.25 (2σ)[3]	von Quadt et al. (2014)	30	55	24.42 ± 0.64 (1σ)	2.7	μ = -4.48 σ = 1.06	-8.3 -1.12 -0.14	1.9	3.0
029-5[5]	24.480 ± 0.084 (2σ)[3]	von Quadt et al. (2014)	42	48	24.47 ± 0.79 (1σ)	3.3	μ = -3.10 σ = 0.47	-10.17 -4.31 -1.76	4.7	5.2
059-1[5]	24.57 ± 0.28 (2σ)[2]	von Quadt et al. (2014)	41	36	24.50 ± 0.95 (1σ)	1.1	μ = -3.48 σ = 0.52	-7.87 -2.99 -1.1	3.4	3.8
CTU	34.41 ± 0.26 (2σ)[2]	Watts et al. (2016)	24	18	34.47 ± 0.83 (1σ)	2.1	μ = -3.21 σ = 0.29	-6.65 -3.88 -2.23	4.0	4.2
RCP	34.38 ± 0.32 (2σ)[2]	Watts et al. (2016)	34	18	34.19 ± 0.75 (1σ)	3.1	μ = -3.96 σ = 0.80	-8.38 -1.87 -0.40	2.5	3.3
SRF	34.62 ± 0.37 (2σ)[2]	Watts et al. (2016)	17	17	34.25 ± 0.75 (1σ)	5.1	μ = -4.57 σ = 1.08	-7.92 -1.03 -0.12	1.8	2.9
DG 026	76.41 ± 0.45 (2σ)[3]	von Quadt et al. (2014)	31	34	76.16 ± 1.42 (1σ)	3.0	μ = -3.74 σ = 0.56	-6.65 -2.32 -0.79	2.7	3.1
MM20-EC-109[6]	144.50 ± 0.07 (2σ)[4]	This study	68	n.a.	144.43 ± 3.12 (1σ)	1.6	μ = -4.73 σ = 1.91	-27.16 -0.87 -0.02	3.6	8.8
AvQ 244[7]	333.60 ± 0.66 (2σ)[3]	von Quadt et al. (2014)	17	19	333.64 ± 10.86 (1σ)	12.3	μ = -2.69 σ = 0.82	-25.30 -6.36 -1.34	8.1	10.3

[1]Sanidine ^{39}Ar/^{40}Ar age (Snow and Lux, 1999)
[2]Error-weighted mean of chemically abraded U-Pb dates
[3]Concordia age (CA-ID-TIMS)
[4]Error-weighted mean 5 of 5 zircon crystals analyzed via CA-ID-TIMS
[5]U-Pb dates older than 28 Ma excluded from analysis
[6]U-Pb dates older than 158 Ma excluded from analysis
[7]U-Pb dates older than 360 Ma excluded from analysis
N = Number of analyses
n.a. = Not available
W_1 = first Wasserstein distance
W_2 = second Wasserstein distance

We present analysis of five samples reported in von Quadt et al. (2014), including upper Oligocene andesite/trachy-andesite from Macedonia (248-2, 029-5, and 059-1), upper Cretaceous dolerite from Romania (DG_026), and middle Carboniferous granite from West-Bulgaria (AvQ 244). These samples were also split into non-CA and CA aliquots prior to analysis via LA-ICP-MS. For samples other than 059-1 we use concordia ages from CA-ID-TIMS analyses of between three and six crystals for the crystallization age of each sample (von Quadt et al., 2014; Table 1). For sample 059-1 we used the weighted mean of the CA U-Pb dates. The number of analyses per sample (non-CA or CA) ranged from 17-55 for this dataset (Table 1).

Sample ELM18DVTC-10 is from a Miocene ash-flow tuff from the Pangua Formation in the western United States that has 144 U-Pb dates acquired via LA-ICP-MS (Miller et al., 2022). We use a $^{40}Ar/^{39}Ar$ weighted mean age of 15.7 ± 0.2 Ma (2σ) from the same unit as an estimate of the crystallization age of this sample (sample 592-GV1 of Snow and Lux, 1999). Sample ELM18DVTC-10 was highlighted by Schwartz et al. (2022) who noted the youngest zircon U-Pb dates to be much younger than the accepted $^{40}Ar/^{39}Ar$ age of this unit. Miller et al. (2022) also noted the presence of these young ~~grains~~ zircon and suggested that they may be a consequence of surface contamination from units higher in the section.

Sample MM20-EC-109 is a Lower Cretaceous intermediate ash interbedded within marine carbonaceous mudstone from the Rio Mayer Formation of Argentina with 68 zircon U-Pb dates acquired via LA-ICP-MS (Table A3~~2~~). Laser ablation spot locations were selected on the rim and/or core of the ~~grain~~ zircon guided by CL images (Figure ~~A2~~A3), with 59 ~~grains~~ zircon crystals analyzed in total ~~analyzed~~. We use a crystallization age of 144.43 ± 0.07 Ma (2σ) derived from a weighted mean ~~average~~ of five zircon crystals analyzed via CA-ID-TIMS at the Boise State University Isotope Geology Laboratory (Table A4~~3~~). This sample exhibits a large offset between the youngest U-Pb dates acquired via LA-ICP-MS, up to ~60% younger than the CA-ID-TIMS weighted mean.

3.3 Statistical analysis

To evaluate the likelihood that the measured Pb*/U~~U-Pb~~ ~~date~~ distribution could have been drawn from the modeled $(f * g)(t)$, we apply the nonparametric, 1-sided Kolgomorov-Smirnov (K-S) and Kuiper statistical tests that compare the ECDF with the cumulative CDF of $(f * g)(t)$ (Press, 2007). The Kuiper statistic is relatively more sensitive in differences in the tails of the distributions versus the K-S statistic (Vermeesch, 2018a). We reject the null hypothesis that the non-CA U-Pb dates were drawn from $(f * g)(t)$ if the K-S or Kuiper p-value is <0.05 (i.e., 95% confidence level). We thus interpret p-values >0.05 to indicate that the non-CA U-Pb dates could have been plausibly drawn from $(f * g)(t)$ at a 95% confidence level (Press, 2007). However, it should be noted that Saylor and Sundell (2016) found that both K-S and Kuiper p-values more frequently reject the null hypothesis than expected. We thus use p-values as a general guideline to model goodness-of-fit.

The Wasserstein distance has been recently proposed as a metric for quantifying the dissimilarity between detrital zircon U-Pb age distributions (Lipp and Vermeesch, ~~in review~~2023). We consider the first and second Wasserstein distances, W_1 and W_2, to be useful approximations for the total degree of negative ~~age~~ Pb*/U perturbation that a set of analyses has experienced,

$$W_1 = \int_0^1 |M^{-1} - N^{-1}| dt \qquad \text{(Equation 3)}$$

$$W_2 = \sqrt{\int_0^1 |M^{-1} - N^{-1}|^2 dt} \qquad \text{(Equation 4)}$$

where M^{-1} and N^{-1} are the inverses of the CDFs M and N. Because values of Pb loss are restricted to between ~~-100% and~~ 0% and 100%, both W_1 and W_2 yield maximum possible values of 100 (i.e., 100% of ~~grains~~ analyses have -100% ~~age~~ Pb*/U offset, or the U-Pb system is completely reset). The W_1 simply equates to the area beneath the cumulative probability distribution of *g(t)*~~the apparent Pb loss function~~ (e.g., Fig. 3). Because the W_2 distance involves a squaring of the distance between the quantile functions, it imparts a higher cost penalty for the part of the distribution with strongly ~~negative~~ offset values. For example, the W_1 and W_2 distances are equal for a Pb loss function characterized by constant Pb loss (e.g., -3% Pb loss produces W_1 and W_2 values of 3, Fig. 3b~~2~~). However, the W_2 distance is often much larger than W_1 for Pb loss distributions with a heavy tail~~, such as the Pareto distribution~~ (Fig. 3d). As such, the W_2/W_1 ratio provides an approximation of Pb loss distribution asymmetry, with values of 1 indicating constant Pb loss and values >>1 indicating highly asymmetric Pb loss.

4 Results

~~Figure X presents a summary of model misfit for each of the 10 samples and 4 primary distribution types considered (see Appendix A for additional results).~~

Of the four primary types of Pb loss distributions considered (Fig. 3), the logit-normal distribution yielded the lowest average misfit with a value of 3.5, followed by the isolated Pb loss scenario (average of 4.5) and the constant Pb loss scenario (average of 10.5) (Table A2~~; see also Appendix A~~).~~he no Pb loss scenario produced~~

~~The isolated Pb loss scenario also produced the closest match with samples RCP, SRF, DG 026, and AvQ 244.~~

~~isolated Pb loss yielded the lowest average misfit with a value 4.2 (Fig. 4).~~The scenario of no Pb loss~~, however,~~ performed the worst of any scenario that we considered, with an average misfit of 101.31~~97.4~~ (Table A2~~Fig. 4~~). Correspondingly, both K-S and Kuiper p-values for the no Pb loss

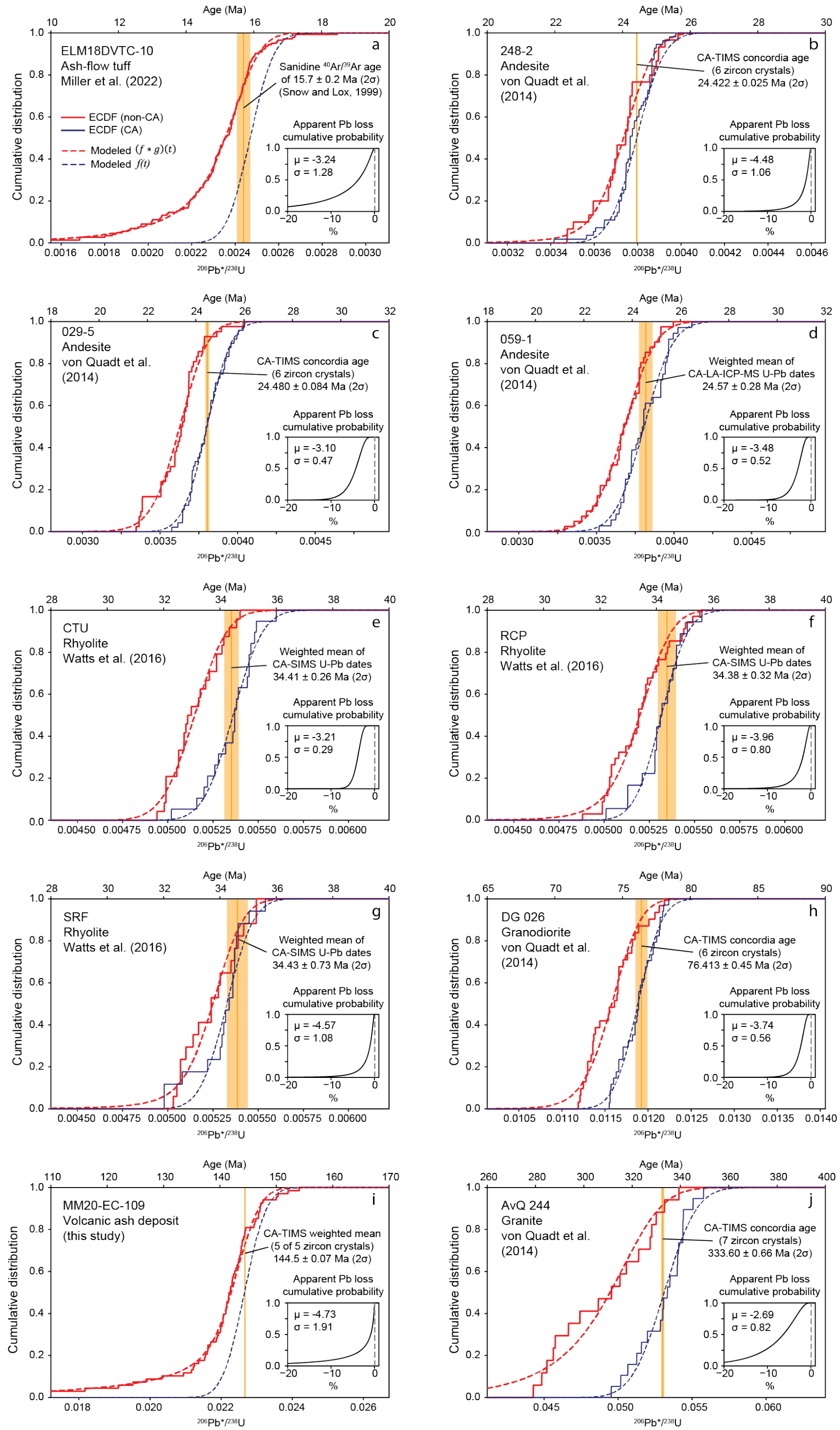

Figure 5. Modeling of apparent Pb loss in zircon U-Pb dates acquired via LA-ICP-MS or SIMS. The best-fitting logit-normal distribution of apparent Pb loss is shown (Table 1; see Figure A1 for plots of all samples and apparent Pb loss distribution types modeled). Empirical cumulative distribution functions (ECDFs) are shown as solid lines while model results are shown as dashed lines. See text for further discussion of model results.

scenario are <<0.05 for all samples except SRF, suggesting that the untreated LA-ICP-MS or SIMS U-Pb dates are unlikely to have been drawn from an unperturbed U-Pb date distribution.~~ Of the continuous distributions considered, the Weibull and lognormal distributions produced the overall best fits, with average misfit values equaling 2.82 and 3.33, respectively (Fig. 4). The Pareto distribution produces a heavy-tail (Fig. 3) that yielded good fits for some samples with extreme outlying values (e.g., ELM18DVTC-10 and MM20-EC-109) but poor fits for some of the other samples (average misfit of 20.1, Fig. 4). The other distribution types yielded intermediate results with average misfit values ranging between 4.8 and 8.1 (Fig. 4). With a few exceptions, p-values for both the K-S and Kuiper tests are >0.05 for the continuous distribution types we modeled (Table A1).~~

Figure 5 presents a comparison of actual versus~~s~~ modeled U-Pb date distributions for each sample, with the best-fitting logit-normal~~continuous apparent Pb loss~~ distribution shown (Table 1; see Figure A1 for individual plots that show the fit for each sample and distribution type). We chose to not consider discrete distributions of *g(t)*~~apparent Pb loss~~ for the "best" fit because we consider it unlikely that Pb loss (or other processes that cause negative age offsets) would be limited to discrete values (e.g., Fig. ~~2~~3). Values of μ *for g(t)* ranged from -2.69 to -4.73 with corresponding values of σ spanning 0.29 to 1.91. ~~The best-fitting continuous distribution types include the gamma (ELM18DVTC-10), Weibull (248-2 and SRF), lognormal (029-5 and 059-1), uniform (CTU), half normal (RCP), and Pareto (MM20-EC-109) distributions (Table 1).~~ W_1 distances ranged between 1.8~~0.9~~ (sample SRF) and 8.1~~7.7~~ (sample AvQ 244) and W_2 distances between 2.9~~0~~ and 11.1~~10.34~~ (Table 1; Fig. 5).~~ In general, the Pareto, gamma, Weibull, and lognormal distributions are more likely to predict more abundant extreme values of age offset than the Rayleigh or uniform distributions (Fig. 5, Table 1, Fig. A2).~~

~~To further examine variations in~~ g(t)~~the distributions of apparent Pb loss between samples, we~~A ~~plotted~~ plot of the best-fitting logit-normal ~~Weibull~~ distributions ~~(Fig. 6). Even though the Weibull distribution was not the closest match for each sample, it yielded the best overall matches across samples, with misfit values <10 for all samples (Fig. 4). Figure 6~~ displays two distinct behaviors of *g(t)* (Fig. 6)~~apparent Pb loss when modeled using the Weibull distribution~~. (1) Four s~~S~~amples with $\mu < \sim -3$ and $\sigma > 1$ and ~~Weibull shape parameter <1~~ have a *g(t)*~~their~~ maximum relative probability ~~of apparent Pb loss~~ close to 0% suggesting a strongly decaying rate of ~~age~~ offset (i.e., most zircon experienced very little Pb loss~~ perturbed U-Pb dates have very little age offset~~, while a few have more significant Pb*/U offset). These samples also displayed $W_2/W_1 \geq 1.6$~~7~~. (2) The remaining six s~~S~~amples that yielded~~with~~ $\sigma < 1$ and generally higher μ values (>-4) ~~a Weibull shape parameter >1, however,~~ displayed~~y~~ a tendency for the mode of *g(t)* ~~apparent Pb loss~~ to be >0%, representing more of a bulk shift in age (e.g., most U-Pb dates have some ~~age~~ offset, while relatively few have very little or very much age offset). These samples ~~that~~ produced $W_2/W_1 \leq 1.3$.

5 Discussion

5.1 Assumptions and limitations

The mathematical and modeling framework that we present includes several underlying assumptions and limitations that should be considered.

1. Because *g(t)* could represent any geological or analytical process that introduces negative age offsets, we use the phrase "apparent Pb loss" when describing our modeled estimates of *g(t)*. For instance, matrix-related systematic errors (Allen and Campbell, 2012), addition of U-Th during weathering (Pigdeon et al., 2019), and even sample contamination from younger minerals could introduce negative age shifts exclusive of loss of radiogenic Pb. Common Pb corrections, particularly the ^{207}Pb-correction, may also introduce a bias towards artificially low Pb*/U values (Anderson, 2002; Anderson et al., ~~Anderson et al.,~~ 2019). We recommend that these additional complexities in the U-Pb system be considered when interpreting modeled estimates of *g(t)* as representing distributions of Pb loss.

2. Our approach of parameterizing ~~of~~ *g(t)* for the purpose of exploratory modeling has the advantage of yielding results that are interpretable while also being suitable for the relatively low-*n* datasets available. However, any parametric model is likely a simplification of the true *g(t)*, and thus we consider our modeled estimates of *g(t)* to be first-order approximations. Analyzing a greater range of samples with a greater number of ±CA *in-situ* U-Pb analyses, with ideal datasets having 100s or even 1000s of analyses per sample (e.g., Pullen et al., 2014; Sundell et al., 2021), would likely improve our ability to constrain the form(s) of *g(t)* and evaluate whether the logit-normal distribution or other forms of *g(t)* are appropriate. Such datasets would also be more amenable to nonparametric solutions of estimating *g(t)*.

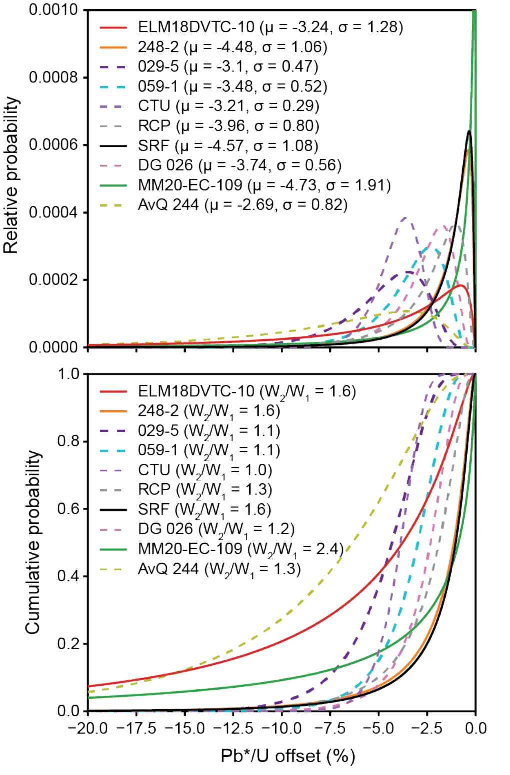

Figure 6. Distributions of apparent Pb loss when modeled as a logit-normal distribution. Samples with σ<1 are shown as a dashed line.

~~2~~3. For *g(t)* to represent the true distribution of Pb loss, the process of convolution must be applied to Pb*/U ratios at the time of Pb loss. Because Pb* is progressively added to the crystal over time, a greater amount of ancient Pb loss is required to achieve the same reduction in Pb*/U relative to recent Pb loss. This point is illustrated in Fig~~.~~ure 1 where a 50% reduction in Pb* at 125 Myr after crystallization produces a similar reduction in ^{206}Pb*/^{238}U when compared to ~~the same grain~~zircon of the same age that lost 25% of its Pb* at 250 Myr (present day). For this reason, *g(t)* can be viewed as a minimum estimate in the case of ancient Pb loss. If the timing of Pb loss is known or can be estimated (e.g., Morris et al., 2015), the input Pb*/U ratios can be adjusted prior to analysis such that *g(t)* more accurately reflects the true magnitude of Pb loss.

4. The modeling framework presented above is designed for a group of cogenetic crystals with a shared crystallization age (e.g., autocrystic zircon from the same magmatic episode; Miller et al., 2007). This requirement stems from our definition of apparent Pb loss as a relative shift, or percentage deviation from the ~~crystallization age~~true isotopic value (Fig. 2~~1~~). The assumption that all zircon are coeval is a simplification, as even autocrystic zircon crystallize over a period of time, typically ~~on~~ 10^3-10^4 yr timescales (Miller et al., 2007; Rossi~~n~~gnol et al., 2019). Multimodal detrital samples or igneous samples with xenocrystic or inherited zircon are not easily modeled because these samples would violate our assumption of a shared crystallization age. Failure to recognize the true heterogeneity in crystallization age in such a sample could cause an incorrect interpretation of the apparent Pb loss distribution.

~~1. When modeling apparent Pb loss via convolution we make the assumption that the amount of age offset is uncorrelated with crystallization age. We consider this to be a reasonable assumption for zircon crystals of similar age and with a shared history (e.g., most igneous samples). However, the relative amount of Pb loss experienced by zircon of different ages could be variable. Older zircon have experienced more radioactive decay and thus are more prone to radiation damage (Marsellos and Garver, 2010). Similarly, some zircon incorporate elevated concentrations (>1000 ppm) of U into their crystal structure, which promotes accelerated radiation damage and degrades the zircon matrix (White and Ireland, 2012). In particular, Pb loss is believed to be most common at temperatures below ~250°C, at which radiation damage cannot be healed (Schoene, 2013). Thus, detrital samples with zircon of widely varying age and provenance are more likely than igneous samples to violate the assumption that Pb loss is independent of age. We consider some strategies for analyzing detrital zircon below in Section 5.3.~~

~~2.~~5. For datasets with paired non-CA and CA measurements, our modeling approach assumes that the relative precision of the analyses is similar. This is because the Gaussian distribution that best approximates the CA U-Pb date distribution, *f(t)*, is convolved with the apparent Pb loss distribution *g(t)* to fit the non-CA U-Pb date distribution. The Watts et al. (2016) SIMS dataset shows similar relative precision regardless of treatment approach (non-CA versus CA). Some samples from the von Quadt et al. (2014) LA-ICP-MS dataset exhibit slightly lower relative precisions for non-CA versus CA, with sample AvQ 244 yielding the largest difference with an average relative precision of 1.1% (1σ) for non-CA dates and 0.8% (1σ) for CA dates. We suggest that for the purposes of modeling apparent Pb loss, paired non-CA and CA U-Pb datasets should be collected on the same instrument using similar acquisition parameters to avoid introducing large changes in measurement precision. Alternatively, the CA U-Pb dates may be used to only constrain the μ of f(t) in the model, with σ treated as an unknown parameter (e.g., for paired non-CA LA-ICP-MS and CA-ID-TIMS datasets; Figs. 5a and 5i).

~~4.~~6. For datasets with paired non-CA and CA measurements, we do not ~~take into account~~consider any imperfections of the chemical abrasion process. For example, although the CA treatment aims to completely remove all radiation damaged zones of the crystal (Mattinson, 2005), it is possible to have remaining residual zones of Pb loss following treatment (e.g., Schoene et al., 2010). Any such remaining compromised domains of the crystal will yield at least some apparent Pb loss when analyzed. For instance, Watts et al. (2016) interpreted three zircon U-Pb analyses from SRF to have some residual Pb loss that was not fully accounted for by the CA process (Fig. 5g). Incorporation of Pb loss-perturbed U-Pb dates when modeling *f(t)* would likely produce an underestimate of the true magnitude of the apparent Pb loss. ~~Additionally, the CA process may itself damage grains to the point of being unrecoverable for future steps (e.g., mounting, analysis). Because loss of grains via CA is likely to correlate with age, geochemistry, and/or history (e.g., older, highly metamict, or recycled grains), there is a potential for differences between the non-CA and CA U-Pb date distributions that do not relate to apparent Pb loss. Analyzing a dataset with a metamict-prone age fraction could result in such differences being mistakenly interpreted as the result of apparent Pb loss if a particular group of zircon are selectively removed by CA. We suspect that this issue may be more prevalent in detrital samples that exhibit greater diversity in zircon characteristics than in igneous samples.~~

5.2 Distributions of apparent Pb loss

What distribution type(s) characterize apparent Pb loss in natural samples? Our results strongly suggest that at least nine of the 10 samples modeled have at least some systematic negative ~~age~~ offset in $^{206}Pb^*/^{238}U$ that cannot be explained by random measurement uncertainties alone. This is because the K-S and Kuiper statistical tests are unable to reject the null hypothesis for many of the apparent Pb loss distribution types considered (Table A1). For example, only the no Pb loss scenario produced a *p*-value <0.05 for sample MM20-EC-109, suggesting that any of the other ~~10~~ modeled distributions of apparent Pb loss may be statistically plausible for this sample. These results suggest that we cannot confidently distinguish between discrete (constant or isolated) or continuous distributions of apparent Pb loss in the datasets modeled. ~~With the exception of~~Except for ELM18DVTC-10 which has 144 non-CA LA-ICP-MS analyses, the samples we analyzed have relatively low numbers of analyses (between 17 and 68, average of 32) for a given sample and treatment category (non-CA or CA) (Table 1). We ~~hypothesize~~ suspect that collection of larger-*n* datasets would allow better ~~differentiation~~ resolution of which parameterizations of *g(t)* might be most appropriate~~between possible apparent Pb loss distribution types, particularly because different distributions can produce similarly looking functions (Fig. 3)~~. ~~In some cases, different distribution types can produce identical probability density functions (e.g., the Weibull distribution interpolates between the exponential and Raleigh distributions).~~

Even if the specific distribution type(s) that characterizes ~~*apparent Pb loss*~~*g(t)* cannot be uniquely identified, our analysis suggests two contrasting behaviors in apparent Pb loss (Fig. 6). We speculate that U-Pb dates that undergo a bulk shift (i.e., $W_2/W_1 \cong 1$) may reflect a population of zircon crystals with relatively homogenous characteristics (e.g., size, U content, etc.) that have all experienced a similar post-crystallization history. Correspondingly, the population of zircon that produces U-Pb dates with a highly asymmetric distribution of age offset (i.e., $W_2/W_1 > \sim 1.5$) may reflect heterogeneity between crystals, with variable characteristics~~ and/or post-crystallization histories~~. For example, Pb loss is thought to be promoted in small zircon crystals and in zircon with elevated U (Ashwal et al., 1999; Gehrels et al., 2020), and thus distributions of particle size and/or trace element geochemistry may ~~play a role in influencing~~influence asymmetric patterns in *g(t)*. Collection of size measurements and trace element concentrations from zircon in addition to measurement of the U-Pb date (e.g., Watts et al., 2016)~~,~~ would likely help evaluate hypotheses about the underlying factors that ~~control~~ influence ~~such behavior of~~ apparent Pb loss distributions. Furthermore, given the relatively small number of samples modeled in this study, we suggest that there is a need for more samples to undergo paired non-CA and CA characterization to improve understanding of the range of behaviors that may be typical. For example, it is presently unclear whether it is more common for samples to have their U-Pb dates bulk shifted (e.g., samples 029-5, 059-1, CTU, DG_026) versus having relatively few U-Pb dates highly offset (e.g., samples MM20-EC-109 and ELM18DVTC-10; Fig. 5).

Why do some samples experience more overall apparent Pb loss than others? Although we anticipated that apparent Pb loss would be greater for older samples, our analysis shows no clear trend by sample age (although we acknowledge that the relatively high degree of apparent Pb loss modeled in the youngest sample, ELM18DVTC-10, may be a consequence of contamination from overlying units, instead of true Pb loss; Miller et al., 2022). Even the three samples from the same Eocene caldera system (CTU, RCP, and SRF) showed contrasting amounts of apparent Pb loss (W_2 ranges from 2.9~~0~~ to 4.~~1~~2; Table 1) as noted by Watts et al. (2016). Characterizing the overall magnitude of apparent Pb loss in a wider range of samples would likely help elucidate predictive factors, if any.

~~5.3 Detrital and other multi-modal samples~~

~~The modeling framework presented above is designed for a group of cogenetic crystals with a shared crystallization age (e.g., autocrystic zircon from the same magmatic episode; Miller et al., 2007). This requirement stems from our definition of apparent Pb loss as a relative shift, or percentage deviation from the crystallization age (Fig. 1). Because detrital samples are typically multi-modal (i.e., zircon are derived from >1 underlying Gaussian distribution), we cannot usually assume that the measured U-Pb dates were all drawn from the same Gaussian distribution,~~ ~~*f(t)*~~~~. For example, volcanic arcs crystallize zircon over the span of 10's of millions of years through multiple cycles of magmatism (Paterson and Ducea 2015). Thus, a detrital zircon age spectra with a volcanic arc source may appear as a broad distribution of U-Pb dates that are themselves multimodal or yield~~

~~distribution tails representing waning magmatic fluxes (Caricchi et al., 2014). Failure to recognize the true heterogeneity in crystallization age in such a sample could cause an incorrect interpretation of the apparent Pb loss distribution.~~

~~However, a sample with zircon crystals derived from multiple Gaussian distributions (e.g., detrital samples or igneous samples with antecrystic, xenocrytic, or inherited zircon; e.g., Rossignol et al., 2019) may also be modeled using this approach provided that the unperturbed U-Pb date distribution (e.g., CA-LA-ICP-MS or CA-SIMS) can be unmixed into its constituent Gaussian distributions (e.g., Sambridge and Compston, 1994). We illustrate this approach in Figure 7 where synthetic U-Pb dates are drawn from a mixture of three Gaussian distributions and convolved with the same Weibull distribution of apparent Pb loss. The resulting Pb loss-perturbed U-Pb date distribution (e.g., non-CA LA-IC-MS or SIMS) can be produced by separately convolving each Gaussian distribution with the Pb loss distribution, *g(t)*, multiplying by the appropriate weighting factor, and then summing them up to unity (Fig. 7b). By modeling 1,000 synthetic U-Pb dates drawn from both the unperturbed and perturbed distributions, we found a modeled *g(t)* (scale = 4.6, shape = 1.3) that was a close match for the true *g(t)* (scale = 5, shape = 1.5) (Fig. 7c). In practice, one could apply this approach by conducting Gaussian mixture modeling on a CA-LA-ICP-MS or CA-SIMS dataset and then convolving each Gaussian separately with the apparent Pb loss distribution when minimizing the misfit.~~

~~One word of caution with this approach is that our modeling framework assumes that the degree of age offset is independent of the age of the sample (see also point #1 in Section 5.1). To counteract this potential issue, we suggest that a U-Pb date distribution with age modes that span a significant reach of time be broken up into groups and modeled separately. In this way, the apparent Pb loss distribution that characterizes a young age mode would be allowed to vary from the apparent Pb loss distribution that has affected an older age mode.~~

5.34 Importance of quantifying the distribution of apparent Pb loss in *in-situ* U-Pb geochronology

The overwhelming majority of published *in-situ* U-Pb dates from zircon, minimally >600,000 and likely in the millions of analyses (Puetz et al., 2021), have not been treated using CA. In contrast, CA is now practiced routinely in the ID-TIMS community which has contributed to growing precision and accuracy over the past two decades (Schoene, 2013). However, the strategy of mitigating Pb loss through avoidance is perhaps less easily adopted to routine *in-situ* U-Pb ~~geochronology.~~ geochronology. For instance, there may be practical limitations with chemically abrading large numbers of zircon crystals~~grains~~, including the potential loss of certain age modes that would be detrimental to provenance analysis. We thus suggest that there is a pressing need to improve quantitative characterization of apparent Pb loss distributions in non-CA *in-situ* U-Pb datasets to aid in interpreting these datasets and to guide strategies for future data collection.

It is somewhat concerning that nine of the 10 samples analyzed in this study exhibited statistically significant amounts of negative age offset from the estimated true crystallization age. Even a small age offset of a few percent, or cryptic Pb loss (Kryza et al., 2012; Watts et al., 2016), has potentially important repercussions for interpreting the age and rates of geologic events and processes. For example, there is a growing awareness in the detrital geochronological community that the youngest zircon U-Pb dates often skew unexpectedly young relative to the plausible crystallization age (e.g., Herriot et al., 2019; Gehrels et al., 2020; Schwartz et al., 2022). Presently, there is no consensus on the importance of post-depositional Pb loss on influencing depositional age interpretations (e.g., Herriott et al., 2019; Copeland, 2020; Schwartz et al., 2022). Sample MM20-EC-109 illustrates the risk well; we initially interpreted the young tail on the U-Pb date distribution to suggest a depositional age of ~125 Ma based on the youngest cluster of overlapping U-Pb dates. The youngest single analysis was a 60.5 ± 2.4 Ma rim on a 135.3 ± 3.0 Ma core, with the second youngest being a 79 ± 1.2 Ma date measured from the core of a ~~grain~~zircon crystal, with the corresponding rim yielding an older 129.8 ± 3.6 Ma date (Table A2). Interpretation of the youngest single U-Pb date or dates as the depositional age of this sample would have produced a highly erroneous estimate, off by up to -58% of the true eruption age of 144.50 ± 0.07 (2σ) Ma as determined by CA-ID-TIMS. Because this ash is interbedded within a sequence of organic rich marine mudstone in the Austral Basin of Argentina, the misinterpretation in this case could have led to an erroneous depositional age model with implications for interpreting the paleoclimatic and geodynamic context of these sediments.

Although modeling detrital samples was outside of the scope of this study, we believe that our results bear upon maximum depositional age analysis. The tendency for the youngest U-Pb dates in a sample to be affected by Pb loss (or other similar process) complicates even conservative estimates of the maximum depositional age (Dickinson and Gehrels., 2009; Coutts et al., 2019; Schwartz et al., 2022). If apparent Pb loss follows a continuous distribution (e.g., Fig. 3d), then it is ill-advised to assume that outlying U-Pb dates may be rejected while the rest are considered unperturbed (see also discussion in Copeland, 2020). Even an interpretation based on the peak age probability of the youngest age mode is likely to be too young, because the process of convolution produces a ~~young-shift~~young shift in the mode of the distribution, in addition to creating a young tail (Fig~~s~~. 3d; Fig. A1~~ and 7~~). Because existing methods of calculating the maximum depositional age (Dickinson and Gehrels, 2009; Coutts et al., 2019; Vermeesch, 2021) do not~~fail to~~ account for systematic negative age offsets, our analysis suggests that there is a higher probability for erroneous estimates of the maximum depositional age if (1) there are a large number of zircon crystals with crystallization ages that are close to the age of deposition, (2) the overall number of measured U-Pb analyses is very high, and/or (3) the magnitude of apparent Pb loss is high. In addition, a heavy-tailed ~~the~~ distribution ~~type~~ of apparent Pb loss (i.e., $W_2/W_1 >> 1$) will result in a greater ~~(e.g., heavy-tailed vs not) will also influence maximum depositional age calculations due to varying~~ probability of finding extremely offset Pb*/U values~~, with samples with large W_2 values particularly at risk of highly inaccurate estimates~~.

~~5.5 Strategies for future data collection~~

~~Given the limitations of existing samples in modeling apparent Pb loss distributions, we suggest two strategies that might guide future data collection. First, increasing the number of analyses would provide improved characterization of the apparent Pb loss distribution. In particular, heavy-tailed distributions (e.g., Pareto) predict rare but highly offset values that may not be identified unless a sufficient number of grains are analyzed.~~ ~~**We suggest that future work focus on increasing the number of ±CA *in-situ* U-Pb analyses, with ideal datasets having 100s, or even 1000s, of analyses per sample (e.g., Pullen et al., 2014). Such efforts are likely to be promoted by recent advances in the rate of LA-ICP-MS throughput for improved provenance characterization of detrital zircon (Sundell et al., 2021).**~~

~~Second, increasing the precision of U-Pb date measurements will facilitate accurate identification of the apparent Pb loss distribution (Fig. 8). As the standard deviation of the unperturbed U-Pb date distribution becomes increasingly small (i.e., due to increasing analytical precision), the convolution of $f(t)$ and $g(t)$ will become increasingly similar to $g(t)$ (Fig. 8). Thus, the same distribution of apparent Pb loss will be more easily discerned for higher precision U-Pb data than for lower precision data. *In-situ* zircon U-Pb dates typically have 1-3% relative uncertainties (Schaltegger et al., 2015; Sharman and Malkowski, 2020), similar to the 'moderate' precision example in Figure 8, whereas the precision achieved by CA-ID-TIMS is commonly better than 0.1% depending on U content and age of the crystal (Schaltegger et al., 2015). Thus, the ideal dataset would consist of large numbers of paired non-CA- and CA-ID-TIMS measurements from randomly selected zircon from the same sample. However, given the practical limitations of cost and time involved with collecting CA-ID-TIMS measurements, we suggest that ±CA-LA-ICP-MS analysis might offer the best compromise between data quantity (i.e., rapid analysis) and precision.~~

~~Figure 8 also illustrates the challenge of accurately identifying the distribution of apparent Pb loss when the degree of Pb loss is small in comparison to the relative precision of the U-Pb dates. For instance, a sample with low amounts of apparent Pb loss (e.g., SRF; Fig. 5) may be equally well modeled by any number of distribution types, as they all are able to collapse to W_1 and W_2 values approaching 0. Thus, we anticipate the ability to differentiate between apparent Pb loss distribution types to decrease as the magnitude of apparent Pb loss decreases, except for perhaps the highest resolution U-Pb datasets (e.g., ID-TIMS). However, this limitation may be partly overcome by increasing the number of analyses per sample.~~

6 Conclusions

This study presents a ~~novel~~ mathematical framework for quantifying the distribution of apparent Pb loss on U-Pb date distributions, which could include true loss of radiogenic Pb or other processes that also produce a systematically negative age offset. We show that a Pb loss-perturbed U-Pb date distribution from a set of zircon crystals with a shared crystallization age can be represented by the convolution of ~~the~~ a ~~unperturbed~~ Gaussian distribution that reflects measurement uncertainty in Pb*/U~~U-Pb date distribution and~~ with ~~the~~ a distribution that characterizes ~~of~~ Pb loss, $g(t)$. Our approach relies on analyzing differences between the untreated ~~date~~ Pb*/U distribution from *in-situ* U-Pb geochronology (i.e., LA-ICP-MS or SIMS) and an independent estimate of the true crystallization age, which could include U-Pb dates from a thermally annealed and chemically abraded aliquot of the same sample or from another geochronometer (e.g., $^{40}Ar/^{39}Ar$). We suggest that the first and second Wasserstein distances (W_1 and W_2) of the apparent Pb loss distribution can be used to quantify the total degree of apparent Pb loss that a set of ~~grain~~ zircon analyses has undergone, with maximum possible W_1 and W_2 values of 100.

We apply this modeling framework to ten igneous samples (Miocene to Carboniferous) analyzed with LA-ICP-MS or SIMS. All but one of the samples showed a high probability that the untreated U-Pb date distribution has been perturbed by Pb loss or other equivalent process. Although our analysis shows that multiple parameterizations of *g(t)* can achieve statistically acceptable fits (i.e., K-S or Kuiper *p*-value >0.05), we suggest that the logit-normal distribution may be a reasonable choice for exploratory modeling of apparent Pb loss distributions. ~~Of the eight types of continuous apparent Pb loss distributions that we considered, the Weibull distribution produced the overall best-fit.~~ However, we caution that the number of analyses in the samples we analyzed was generally low (17-144, average of 39~~),~~); future efforts to characterize *g(t)* may be promoted by collection of larger-*n* datasets and through development of nonparametric methods of estimating *g(t)*. Furthermore, our estimates of *g(t)* should be viewed as minimum estimates of the true amount of Pb lost, as we assumed present-day Pb loss in our analysis. These caveats aside, ~~which likely contributed to many of the modeled Pb loss distributions producing statistically acceptable fits (i.e., K-S or Kuiper p-value >0.05). In general,~~ we noted two behaviors of apparent Pb loss ~~in these samples~~; samples with a bulk shift in U-Pb date distributions (W_2/W_1 <~1.3) and samples where most ~~grains~~ analyses had very little offset but fewer ~~grains~~ had much larger offsets (W_2/W_1 >~1.~~7~~6). The overall magnitude of ~~apparent Pb loss~~Pb*/U decrease was also found to be variable, with median values varying from -0.9% to -6.~~5~~4%.

~~Although our modeling framework is designed for analysis of cogenetic grains, and thus most appropriate for igneous samples, we illustrate how the approach could be applied to detrital samples by first unmixing the CA U-Pb date distribution into component Gaussian distributions. However, analysis of detrital samples with zircon of widely varying age and history may violate an assumption of our model that the amount of apparent Pb loss is uncorrelated with age. We thus suggest that multimodal U-Pb date distributions be divided and modeled separately to allow the apparent Pb loss distribution to vary over time.~~

Given the widespread application of *in-situ* U-Pb geochronology of untreated zircon across many disciplines of geosciences, improved characterization of both the distribution type(s) and magnitude of apparent Pb loss is warranted, particularly for Phanerozoic zircon where cryptic Pb loss is difficult to identify. We highlight a need for increased sampling and high-*n* characterization of paired non-CA and CA *in-situ* U-Pb datasets. ~~±CA-LA-ICP-MS in particular has potential given the ability to rapidly acquire the type of large datasets that would facilitate modeling apparent Pb loss distributions.~~ In addition, we recommend simultaneous collection of parameters such as zircon size and trace elemental concentrations to aid in future efforts to understand the mechanisms of negative age offsets. Ultimately, we anticipate that improved characterization of the magnitude ~~and distribution type(s)~~ of apparent Pb loss will aid in interpreting non-CA *in-situ* U-Pb datasets and guide strategies for future data collection.

Data availability

Data are archived under https://doi.org/10.5281/zenodo.8302521~~https://doi.org/10.5281/zenodo.7783226~~. Appendix A provides a description of exploratory modeling of different parameterizations of $g(t)$. Figure A1 includes examples of eight continuous distribution types not explored in the main text. Table A1 and Figure A2 include ~~Table A1 and Figure A1 include~~ summaries of all model results. Table A2 presents a summary of model fit for each sample and distribution type considered. Tables ~~A2~~ A3 and ~~A3~~ A4 provide U-Pb analytical results for sample MM20-EC-109 from the University of Arizona LaserChron Center (LA-ICP-MS) and Boise State University Isotope Geology Laboratory (CA-ID-TIMS), respectively. Figure ~~A2~~ A3 includes CL images from the University of Arizona LaserChron Center. ~~Figure A3 provides a summary of all best fitting continuous Pb loss distributions for each sample.~~Supplemental Video 1 provides an example of convolution. Supplemental Video 2 presents an exploration of the parameter space for the logit-normal distribution.

Code availability

Code used in this research is available on GitHub (https://github.com/grsharman/Pb_loss_modeling) with the ~~initial~~ v2.0.0 commit archived under https://doi.org/10.5281/zenodo.~~7783243~~8302313.

Video supplement

Supplemental Video 1 is available at https://doi.org/10.5281/zenodo.8302521~~https://doi.org/10.5281/zenodo.7783226~~. This animation provides an illustration of how a Gaussian distribution of U-Pb dates (solid, blue line), $f(t)$, may be perturbed by ~~exponential~~ logit-normal Pb loss, $g(t)$ (solid, red line). The ~~exponential~~ Pb loss distribution is first reflected about the y-axis and then iteratively shifted by small values of t, $g(t\text{-}\tau)$ (dashed, red line). The convolution of $f(t)$ and $g(t)$ at any given value of t equals the summed area underneath the product of $f(t)$ and $g(t\text{-}\tau)$. Supplemental Video 2 is also available at https://doi.org/10.5281/zenodo.8302521 and illustrates how the logit-normal distribution varies with respect to its two parameters μ and σ. Note that we have rescaled the x-axis of the logit-normal distribution such that $-100<x<0$.

Author contribution

G. Sharman and M. Malkowski co-designed the study. G. Sharman developed the code. M. Malkowski produced the U-Pb data from sample MM20-EC-109. G. Sharman and M. Malkowski wrote the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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