https://doi.org/10.5194/gchron-2024-27
Preprint. Discussion started: 28 October 2024

GEOCHRONOLOGY Discussions Open Access EGU

Discordance Dating: A New Approach for Dating Sedimentary Alteration Events

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Abstract:
Zircon is the premier geochronometer used to date igneous and metamorphic processes, constrain sediment provenance, and monitor key events in Earth history such as the growth of continents and the evolution of the biosphere. Zircon U-Pb systematics can be perturbed by the loss or gain of uranium and/or lead, which can result in disagreement between the apparent radiometric ages of the two U-Pb decay systems – a phenomenon that is commonly termed ‘discordance’. Discordance in zircon can be difficult to reliably interpret and therefore discordant data are traditionally culled from U-Pb isotopic datasets, particularly detrital zircon datasets. Here we provide a data reduction scheme that extracts reliable age information from discordant zircon U-Pb data found in detrital zircon suites, tracing such processes as fluid flow or contact metamorphism. We provide the template for data reduction and interpretation, a suite of sensitivity tests using synthetic data, and ground-truth this method by analyzing zircons from the well-studied Alta Stock metamorphic aureole. Our results show accurate quantification of a ~23 Ma in situ zircon alteration event that affected 1.0-2.0 Ga detrital zircons in the Tintic quartzite. The ‘discordance dating’ method outlined here may be widely applicable to a variety of detrital zircon suites where pervasive fluid alteration or metamorphic recrystallization has occurred, even in the absence of concordant U-Pb data.

1. Introduction:

U-Pb isotopic compositions of the mineral zircon provide some of the most accurate and precise age information in the geologic record (e.g., Mattinson, 2013, 2005; Schaltegger et al., 2015; Schoene, 2014). U-Pb zircon ages from granitoids have shaped understanding of magmatic processes (e.g. Samperton et al. 2015; Barboni et al. 2015; Schaltegger and Davies 2017). Combining this geochronometer with other chemical information such as Hf-isotope compositions, oxygen isotopic compositions and trace element abundances has advanced understanding of the formation and evolution of continental crust (e.g. Belousova et al. 2010; Roberts and Spencer 2014; Reimink et al. 2023). Zircon is a refractory mineral that also resists chemical and mechanical erosion and persists in sediments over long transport distances (e.g., Reddy et al. 2006). Detrital zircon grains in sedimentary rocks can therefore be used to track sediment provenance, basin dynamics, and the evolution of life (Andersen et al., 2019; Carter and Bristow, 2000; Fedo et al., 2003; Gehrels, 2014; Landing et al., 2021). Indeed, the oldest known fragment of Earth is in a detrital zircon grain (Froude et al., 1983).

https://doi.org/10.5194/gchron-2024-27
Preprint. Discussion started: 28 October 2024

One advantage of the U-Pb system is that it includes two independent decay chains that can be used to internally corroborate the robustness of radiometric ages. ^{238}U decays to ^{206}Pb while ^{235}U decays to ^{207}Pb. A single measurement of the multi-isotopic abundances of U and Pb thus yields multiple dates. When these dates agree within analytical uncertainty, the analyses are termed 'concordant'. 'Discordant' data are cases where the two U-Pb ages disagree, indicating either a mixed-age analytical domain, or that the U-Pb system has been disturbed, either through the gain or loss of U and/or Pb such that the zircon analytical volume was an open system at some point in its history.

Discordant zircon U-Pb data may be created in multiple ways, including pure Pb-loss (Nasdala et al., 1998), uranium addition (Garber et al., 2020; Grauert et al., 1974; Seydoux-Guillaume et al., 2015), a combination of both U gain and Pb loss (Andersen and Elburg, 2022), clustering of Pb into nanoparticles (Kusiak et al., 2015, 2023), mixing between two domains of different ages (Schoene, 2014 and references therein), and partial metamorphic recrystallization (e.g., Davis et al., 1968; Geisler et al., 2007; Hoskin and Black, 2002). Experimental evidence has shown that during the radioactive decay of U and Th, alpha recoil damage accumulates in the crystal lattice and can lead to interconnected pathways that may allow radiogenic Pb to escape the mineral grain and result in discordant U-Pb dates (Geisler et al., 2002, 2007; Salje et al., 1999; Trachenko et al., 2002). Many of these complex processes are difficult to disentangle at the micron scale. In particular, Pb-loss, metamorphic recrystallization, and/or diffusion-reaction processes (Geisler et al., 2007) can prove hard to differentiate from one another at the scale of a typical laser ablation analytical volume (5,000-10,000 μm^3).

Despite the difficulties in understanding the atomic-scale causes of U-Pb discordance in zircon, many geological processes are known to induce discordance, including the buildup of metamict domains inside zircon crystals (Nasdala et al., 1998), meteorite-impact induced shock effects (Moser et al., 2009, 2011) crystal-plastic deformation (Reddy et al., 2006), fluid induced dissolution-reprecipitation (Geisler et al., 2002, 2007), and metamorphic recrystallization and overgrowth that inherits some radiogenic Pb during recrystallization (Mezger and Krogstad, 1997; Schoene, 2014). It has also been suggested that highly radiation damaged zircon crystals may continually lose Pb until they experience an annealing event (Schoene, 2014).

In summary, the atomic-scale mechanics of discordance are not well understood, and most modern U-Pb studies aim to minimize its effect rather than understand or use it (see Schoene, 2014, and references therein). Thus, most studies that leverage the U-Pb system in zircon focus on concordant or upper intercept U-Pb dates (the upper intersection of a regression line through discordant data with the concordia curve) to determine the timescales of mineral formation (e.g., Vermeesch, 2021 and references therein). In fact, the analytical expression of discordance has long been utilized for understanding the events that cause it. This is typically done using linear regressions (Davis, 1982; Vermeesch, 2021; York, 1968) through datasets that fall along a single chord – meaning they have one single upper intercept event (often igneous or metamorphic crystallization) and one single lower intercept event (caused by one of several potential mechanisms, discussed above). Such an approach has yielded meaningful ages for a variety of geological processes (Mezger and Krogstad, 1997; Moser et al., 2009, 2011; Schoene, 2014).

https://doi.org/10.5194/gchron-2024-27
Preprint. Discussion started: 28 October 2024

Sedimentary detrital zircon analyses present a particular difficulty, and as we will show, opportunity, for dealing with discordance when compared to igneous and metamorphic zircon studies. Because each detrital zircon in a sediment may have a unique geologic history, with a correspondingly unique U-Pb disturbance and resetting history, it can be difficult to correctly interpret discordant data from detrital zircon populations. Without the constraint of a single, shared geologic history, no discordant datum can be confidently related to another datum, whether it is discordant or concordant. Therefore, in detrital zircon geochronology, the typical workflow includes discarding any analyses that do not pass a relatively strict discordance filter of 5% or 10% discordant (Gehrels, 2011). At times this can result in a significant number of data being discarded, at times up to more than 60% of the total dataset (e.g., Clemens-Knott and Gevedon, 2023). A limited number of publications have recently focused on improving methods to treat discordant detrital zircon data that would allow for the extraction of useful age information (Andersen et al., 2019; Morris et al., 2015; Olierook et al., 2021; Powerman et al., 2021; Vermeesch, 2021). These include improved filtering and treatment of discordant data (Andersen et al., 2019; Powerman et al., 2021; Vermeesch, 2021) as well as treatments that attempt to project from concordant data in either upper or lower intercepts to the opposite intercept (Morris et al., 2015; Olierook et al., 2021; Reimink et al., 2016).

Despite the difficulty in linking the ages between individual discordant zircon in detrital sediments, one useful assumption can safely be applied: after the deposition of the sediment, all the zircon grains have a shared thermal and geological history. In this study we leverage this assumption that post depositional U-Pb isotopic discordance may affect all zircon grains within a given sediment at the same time, in order to use discordant detrital zircon U-Pb data to investigate post-depositional geologic events (e.g. Morris et al., 2015). We also provide a robust analytical framework for determining the timing of these discordance-inducing events. We empirically show that detrital zircon grains from a sediment that was affected by contact metamorphism and fluid flow can be used to estimate the age of metamorphism and fluid alteration using zircon U-Pb discordance alone. We discuss the potential for this geochronometric tool to be applied to other types of geologic settings in sedimentary settings globally. Because discordance is commonly observed in U-Pb data, but such data are commonly rejected, we suggest that discordance is an undervalued and useful feature of detrital zircon populations, though more work is required to fully evaluate the applicability of our new analytical framework to various discordance-causing geological phenomena.

2. Methods

2.1 Theoretical Framework

Here we date in situ alteration of detrital zircons based on the approach to discordance outlined by Reimink et al. (2016). In this framework, a numerical algorithm is used to calculate the probability distribution of a zircon U-Pb dataset across a range of synthetic discordia chords that represent candidate chords spanning a defined age range. Essentially, a 'mesh' of potential discordia chords is created at a defined interval (e.g., every 1 Ma a new chord is created) wherein each line has a unique upper and lower intercept age (Fig. 1b). Then, the total probability that falls on each chord is calculated by determining the probability that each individual datapoint contributes to each chord, using the equations of (Davis, 1982). The total probability is summed for each chord and termed 'likelihood'. Further details on the method can be found in Reimink et al. (2016).

https://doi.org/10.5194/gchron-2024-27
Preprint. Discussion started: 28 October 2024

Reimink et al. (2016) discussed several different normalization strategies to avoid biasing the calculated probability distributions, including homogenizing the uncertainty across a U-Pb dataset, weighting against concordance (towards discordance), and others. These normalizations can be useful to prevent artificially biasing results due to clusters of concordant data, or biasing due to heteroscedastic data (i.e., with non-uniform variance; Vermeesch, 2012). In detrital zircon datasets from rocks without post-depositional disturbances, the chord with the highest probability is likely to be associated with a group of zircon crystals that have the same upper intercept age, regardless of whether they are discordant or not. In such an analysis, the upper intercept ages the most useful output. Thus, dating a post-depositional discordance-inducing *lower-intercept* event requires a different approach. The present method modifies the original calculations to determine the most likely lower intercept age across a sample set that may have a range of upper intercept ages. For example, using the Reimink et al. (2016) calculation on a detrital sample which has a large population of near-concordant grains at 1600 Ma and experienced a Pb loss event at 30 Ma, the chord with the highest probability would likely be chord between 30 and 1600 Ma (Fig. 1). However, 30 Ma lower intercept ages associated with any other upper intercept age would not be included in the probability of the 30 Ma lower intercept age, as only the 30-1600 Ma chord is considered. If a detrital zircon population contains grains that crystallized at 1000 Ma, 1200 Ma and 2700 Ma and these grains also experienced *in situ* Pb-loss at 30 Ma, that Pb-loss would go mostly undetected by the previous method, though each upper intercept age would be resolved independently.

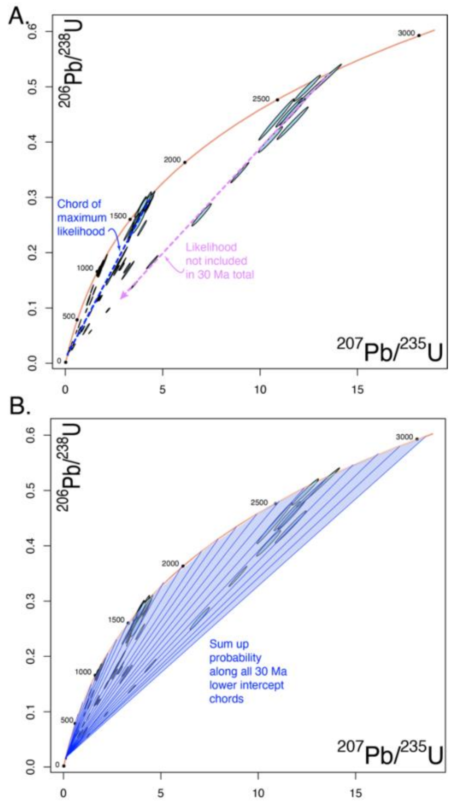

Figure 1: Example data showing why the sum probability density is required to accurately define likelihoods for lower intercept ages. In this synthetic dataset, there are many near-concordant ~1600 Ma datapoints. This cluster of near-concordant data will yield a higher probability for any chord anchored at 1600 Ma. A new method is required to evaluate the total probability contributed to any lower intercept age from a range of upper intercept ages. Panel B shows how the total probability density contributed to all lines with a 30 Ma lower intercept age could capture the likelihood of lower intercept ages in that window.

To rectify this issue, here we introduce a modification to the original calculation. We add an additional step that sums the total probability aggregated to each lower intercept age. Using the example above, we add up all the probability accrued to all the lines with a lower intercept age of exactly 30 Ma. Thus, the probability accumulated by the 30-1580 Ma chord would be added to the probability accumulated by the 30-1581 Ma chord, the 30-1582 Ma chord, etc. This sum is then divided by the number of chords that have a given lower intercept age to normalize across the age range of interest. This value is then termed 'summed likelihood' as it is a normalized value and no longer a probability density estimate. The results of this modeling approach theoretically return an estimate

https://doi.org/10.5194/gchron-2024-27
Preprint. Discussion started: 28 October 2024

of the potential that a given lower intercept age may be a true post-depositional disturbance age, though it is normalized by the number of analyses and number of chords in any given model.

2.2 Calibration with Synthetic Datasets

To test the validity and reliability of our theoretical approach to extracting the ages of post-depositional discordance-inducing events from detrital zircons, we constructed several synthetic datasets and benchmarked our approach against traditional isochron regression techniques. To do this, we used three categories of synthetic datasets (Fig. 2):

1. A U-Pb dataset that defines a perfect discordia line with an upper intercept of 1800 Ma a lower intercept of 30 Ma
2. A dataset with three upper intercept ages (1800 Ma, 1400 Ma, 1100 Ma) all of which have discordance imposed at a shared lower intercept of 30 Ma
3. A dataset where each grain has an upper intercept age randomly selected from a range of ages (1800-1100 Ma) and all have a shared lower intercept of 30 Ma.

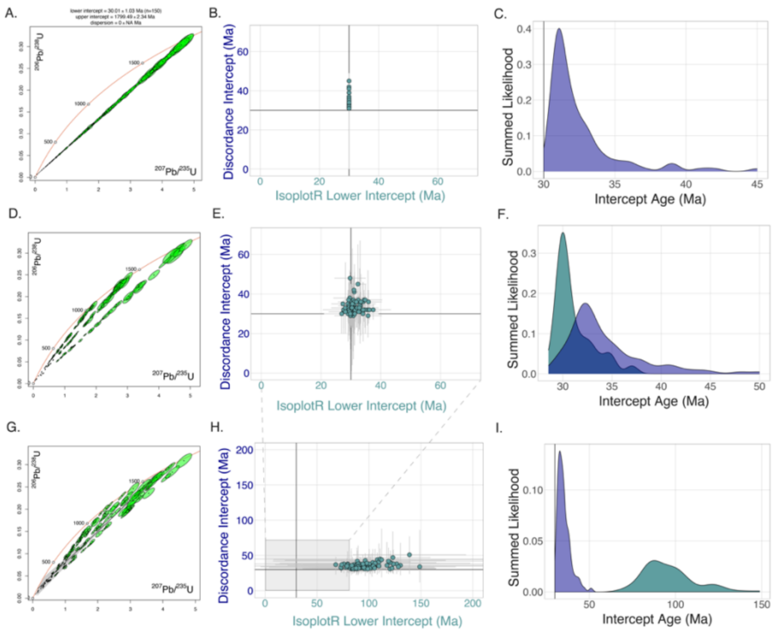

Figure 2: Input data and results from a synthetic data modeling procedure. Panels A, D, and G show examples of the synthetic input data, plotted on U-Pb concordia diagrams. The center panels (B, E, H) show the mean and uncertainties of the Isoplot R regression lower intercept age compared to the lower intercept values derived from the discordance modeling approach. Each data point represents a single synthetically generated dataset of 150 data points. The rightmost pane (C, F, I)l shows the distribution of lower intercept ages from each method with the blue curve representing the ages produced by the discordance model and the green curve representing the ages generated by the model 1 regression in IsoplotR. Note the change of scale in Panel H compared to E and B.

For each of the three categories, a synthetic data population was generated that contained 150 U-Pb data points. Each data point was randomly assigned an upper intercept and lower intercept age based on the model structure. In the case of the perfect line, all data points had the same upper intercept age. Then, each data point was assigned a random amount of discordance between 99.95% and 1%, selected from a flat probability distribution. This random discordance accounts for the fact that each individual zircon grain, and indeed portions of grains, have differing resetting susceptibilities due to a variety of factors. The ratios of interest for each data point were assigned a random uncertainty value between 2-5% of their isotopic composition.

https://doi.org/10.5194/gchron-2024-27
Preprint. Discussion started: 28 October 2024

Each synthetic data set of 150 points was then evaluated in two ways. First, the traditional U-Pb regression ages were derived using the commonly used "York fit" approach (York, 1968) as implemented in IsoplotR (Vermeesch, 2018), from which the upper and lower intercept ages were extracted. For the model constructed with three discrete upper intercept ages, we calculated three independent isochron regressions in IsoplotR, one for each population of synthetic data with a unique upper intercept age, and then calculated the weighted mean lower intercept age of these three regressions. Second, the data were input into our discordance modeling procedure and the maximum sum likelihood was extracted as well as the full width, half max of that peak – a measure of the spread in our modelled spectral data.

This entire procedure was repeated 100 times for each of the three categories, resulting in 300 model runs. The results from the outputs of the 'York fit' approach (model 1 regression in Isoplot R) are compared to our discordance modeling approach. Figure 2 shows the three different types of models, with the calculated lower and upper intercept ages from each individual dataset. Each category of example dataset is synthesized 100 times, and derivative calculations are shown for each type of dataset. Note that in Fig. 2C, the IsoplotR lower intercepts are tightly bound at 30 Ma so the probability density is not shown here. Figure 3 shows the discordance dating outputs in more detail, with individual age distributions shown from the discordance dating outputs. It is important to note that our discordance dating approach makes no assumptions about the distribution of the data and does not require linearity between the data points to perform linear regression calculations. As such, the discordance dating approach is more agnostic with regard to the distribution of the underlying data, and therefore yields more accurate results for complex datasets (Fig. 4). The discordance dating approach can also yield asymmetric likelihood distributions (Fig. 3 center panels) due to the structure of the underlying U-Pb data set.

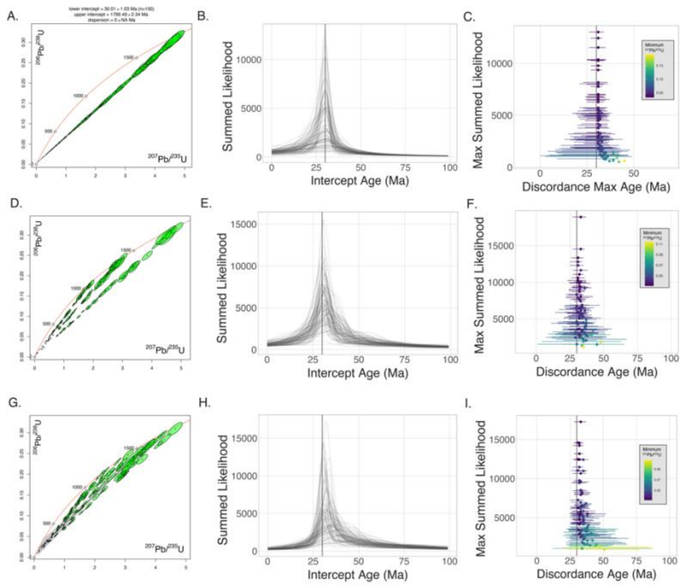

Figure 3: Results from the three sets of model runs for the discordance modeling procedure. The left panels show examples of the input datasets (same as Fig. 2). The central panels show lower intercept likelihood curves for the 100 model runs in each category of model. The right panels show the peak location, the uncertainties (derived by a full-width half-max calculation), and are colored according to the lower $^{207}Pb/^{235}U$ value in a given synthetic dataset. The discordance modeling procedure yields similar results independent of the input data type.

The outputs of each calculation method are summarized in Fig. 4. For the simplest scenario, the perfect discordia line, the IsoplotR York-fitting calculations correctly determine the lower intercept

https://doi.org/10.5194/gchron-2024-27
Preprint. Discussion started: 28 October 2024

age of 30 Ma with excellent precision (mean = +/- 0.33 Ma), while the discordance dating model has larger uncertainties associated with the lower intercept age. As shown in Figure 3, the FWHM of peaks returned by the discordance dating procedure are positively correlated to the peak height, where higher peaks return smaller FWHM uncertainty estimates. Sharp peaks are, in turn, correlated to how close the 'youngest' analysis is to the 30 Ma lower intercept, where precise lower intercept estimates are typically derived from populations of data points that have some analyses close to the concordia curve near the lower intercept age. It is expected – and observed (Fig. 4) – that the York fitting procedure used in IsoplotR should outperform the discordance dating algorithm with respect to precision on the lower intercept for the simplest case where data can be regressed on a single line. However, both methods still recover the accurate lower intercept age within uncertainty.

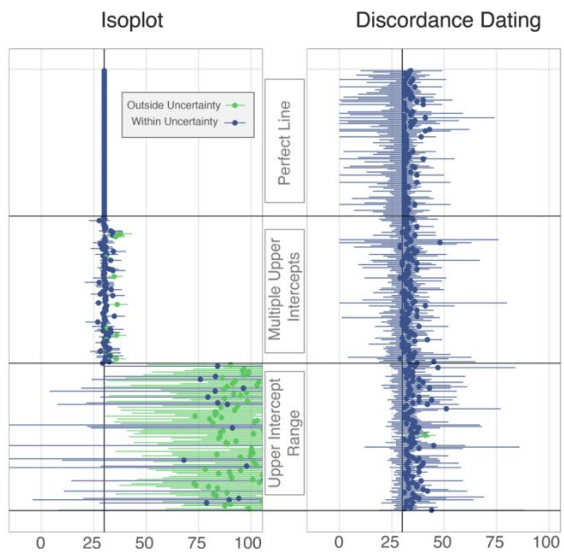

Figure 4: A comparison of the lower intercept ages and uncertainties for the Isoplot regression calculations and the Discordance Dating method for all synthetic data runs. Each point is a unique dataset and the uncertainties are given for each regression point. The color of each point corresponds to whether the lower intercept age is within uncertainty of the pre-defined lower intercept of 30 Ma or not. The Discordance dating method provides more reliable results across a range of data types than simple linear regression models. d

When considering more complex U-Pb populations (for example the lower panels in Fig. 4) that contain many primary (upper intercept) U-Pb ages, the discordance dating procedure outperforms single linear regression and weighted means of multiple linear regressions, as used in Isoplot calculations. In the case of having multiple discrete upper intercept ages (middle panel in Fig. 4), the discordance dating, although less precise, provides improved accuracy and likely a more reliable uncertainty estimate. For the case of many upper intercept ages (lowest panel in Fig. 4) discordance dating is both more accurate (fewer model runs predict lower intercept ages that are outside uncertainty of the 'true' age of 30 Ma – 1/100 for discordance dating, 88/100 for IsoplotR) and more precise than the single line regression.

This is also an expected result. A linear regression method is poorly suited for highly scattered data that do not share a common linear relationship, highlighting the difficulty in extracting valuable U-Pb resetting age information from discordant data. In comparison, the discordance dating method is robust regardless of the nature of the distribution of original U-Pb crystallization ages that experience a shared discordance-inducing event. We interpret this result to support the use of the method for a new approach to evaluate of the distribution of discordant data in U-Pb space.

This exercise also sets expectations for the uncertainties and potential biases on the lower intercept that can be derived from this procedure. Focusing on the models with a range of upper intercept ages, discordance dating returns an uncertainty envelope that is on average ~20 Ma (average peak width using FWHM on each peak). However, the central peak of the discordance dating (the

https://doi.org/10.5194/gchron-2024-27
Preprint. Discussion started: 28 October 2024

maximum likelihood lower intercept age) for these 100 models is 35 Ma +/- 3.4 Ma (1SD). The discordance dating procedure infrequently returns peak centers that are younger than 30 Ma, though it commonly returns peak centers older than 30 Ma. This bias to older lower intercept ages is likely due to the sensitivity of the discordance dating procedure to the position of the youngest point in any dataset – or the most 'reset' grain in any population. This is also important for our later interpretations – discordance dating is highly unlikely to return a max peak position that is too young (assuming no modern-aged discordance in the population), and any maximum peak position can likely be interpreted as a maximum age value for the true lower intercept resetting age.

3. Alta Stock Detrital Zircon Results

3.1 Methods and Results

To test and validate the discordance dating strategy outlined above, we conducted a laser ablation ICPMS analytical campaign targeting a well-studied metamorphic aureole with a known fluid-alteration history. We sampled a metasedimentary unit from the well-studied Alta stock metamorphic aureole, Utah (Brenner et al., 2021; Cook et al., 1997; Moore and Kerrick, 1976; Stearns et al., 2020). The Alta stock intruded a suite of mid-Paleozoic sedimentary rocks in the late Paleogene (36-30 Ma; Stearns et al., 2020 and references therein) and was exposed through Miocene-aged uplift and titling along the Wasatch fault and Pleistocene glaciations and erosion in Little Cottonwood Canyon (Stearns et al., 2020 and references therein). The Alta stock is one of a handful of plutons in the region that formed between ~36 Ma and ~30 Ma (Bromfield et al., 1977; Crittenden et al., 1973; Kowallis et al., 1990; Stearns et al., 2020). Titanite and zircon age constraints from the Alta stock indicate it was emplaced near the early stages of this interval (Crittenden et al., 1973; Stearns et al., 2020). Stock emplacement was accompanied by contact metamorphism in the host units and hydrothermal fluid alteration (Brenner et al., 2021; Cook et al., 1997; Moore and Kerrick, 1976). This fluid flow was primarily down-temperature and was focused in mixed carbonate-siliciclastic beds facilitated by porosity-forming decarbonation reactions (Cook et al., 1997). Previous geochronology on magmatic and overprinted zircon along with magmatic and metamorphic aureole titanite phases indicates Alta stock contact metamorphism extended from >30 to 25 Ma (Stearns et al., 2020). This, in combination with trace-element thermobarometry led Stearns et al. (2020) to conclude that the earliest (36-30 Ma) phases were dominated by high temperature plutonism and metamorphism, whereas hydrothermal alteration activity remained active until ~23 Ma, particularly at the margins of the Alta stock.

We focused on a single sample of the Cambrian Tintic quartzite. This was collected ~200m from the contact with the Alta stock contact, above the tremolite-in isograd, and experienced metamorphic and fluid-alteration temperatures of ~450°C (Brenner et al., 2021; Cook et al., 1997).

https://doi.org/10.5194/gchron-2024-27
Preprint. Discussion started: 28 October 2024

This metamorphic and alteration history, combined with the ages of detrital zircons found in the Tintic formation ranging from 1.0 Ga to <2.5 Ga (Matthews et al., 2017), provides an ideal testing ground for determining the accuracy and precision of the discordance dating technique.

Detrital zircons were isolated using standard crushing and mineral separation practices. Limited hand picking of zircons was conducted in an attempt to avoid biasing the results at that stage. Zircons were selected from other heavy minerals, but no preference was given for quality or morphology of zircon grains at this picking stage. Zircons were mounted in epoxy, polished to midsection, imaged using secondary electron imaging techniques, and subsequently analyzed by laser ablation techniques following the methods of (Cipar et al., 2020; Schoonover et al., 2024). A Teledyne/Photon Machines Analyte G2 excimer laser was used, with a Helex2 ablation cell, for all laser ablation work.

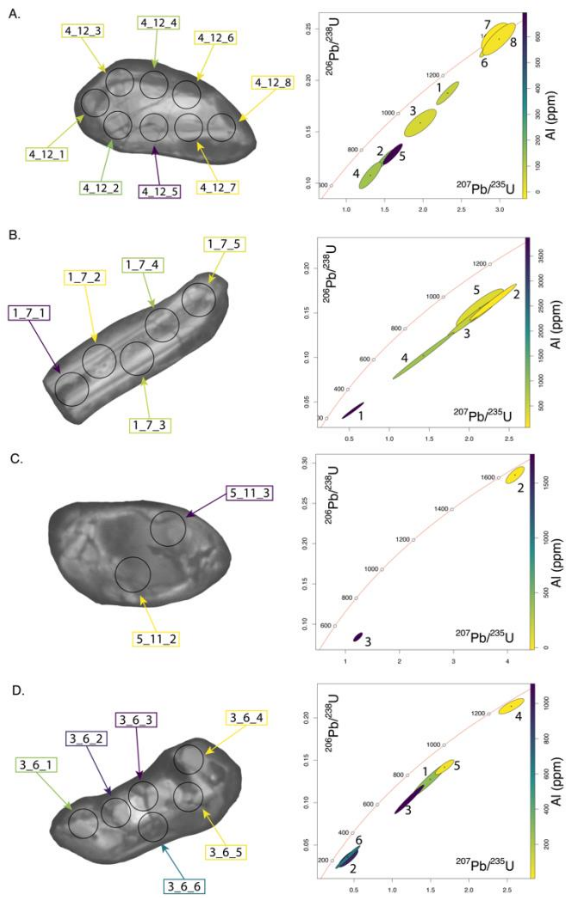

Figure 5: Representative Tintic detrital zircons and their U-Pb isotopic data. Each analysis point is labeled, where color labels correspond to the Al concentration of the analytical volume. The color scales vary between grains. Spot sizes are 30 μm in diameter.

Zircon U-Pb and trace element data was collected in three sessions from Feb. 2023 to May 2023. Two sessions, on Feb. 28th, 2023 and March 3rd, 2023, collected U-Pb-TE on the Thermo Scientific iCapRQ quadrupole mass spectrometer in the LionChron analytical facility. Isotopes measured included ^{27}Al, ^{29}Si, ^{44}Ca, ^{51}V, ^{57}Fe, ^{146}Nd, ^{147}Sm, ^{163}Dy, ^{172}Yb, ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{232}Th, and ^{238}U. The analytical session on May 30th, 2023 utilized split stream techniques, where ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{232}Th, ^{235}U and ^{238}U were analyzed on the Thermo Scientific Element XR ICPMS system and ^{7}Li, ^{23}Na, ^{27}Al, ^{29}Si, ^{31}P, ^{43}Ca, ^{45}Sc, ^{49}Ti, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{119}Sn, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{180}Hf, and ^{182}W were measured on the iCapRQ quadrupole mass spectrometer. ^{235}U was calculated from ^{238}U and the U-isotopic composition of 137.818 (Hiess et al., 2012) due to low ^{235}U signals. NIST 612 glass was used as a trace-element primary reference material and zircon 91500 was used as a primary reference material for U-Pb isotopic measurements. Uranium-lead and trace element data was filtered, standardized, and normalized using the Iolite data reduction software.

https://doi.org/10.5194/gchron-2024-27
Preprint. Discussion started: 28 October 2024

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Secondary zircon reference materials include Piexe, GJ-1, Plesovice, and MudTank. Secondary reference material U-Pb results are shown in the supplements. The only session where a secondary reference material's U-Pb age was > 2% outside of the accepted age was in the March 3rd session, where GJ-1 had an average $^{206}Pb/^{238}U$ age ~3% lower than the accepted age. However, during the same session Piexe returned a $^{206}Pb/^{238}U$ age in line with the accepted age. Position-dependent fractionation may have played a role in the slightly increased inaccuracy of the GJ-1 zircon during this analytical session. All other sessions returned secondary reference material results within 2% of the accepted ages (see supplementary materials for data and results).

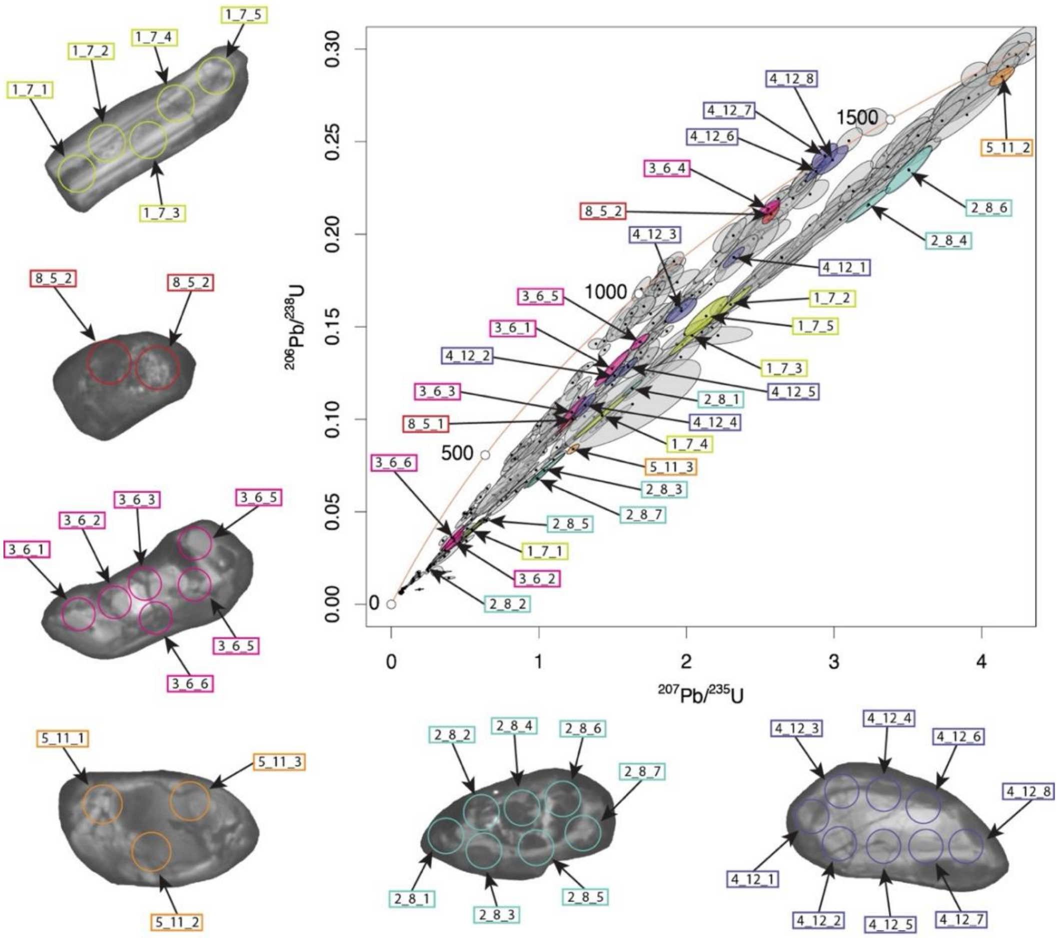

Figure 6: U-Pb data from detrital zircons extracted from the Tintic quartzite sample studied in this work. Zircon secondary electron microscope images are shown with spot locations correlated to individual data points. For scale, laser spots are all 30 µm.

Detrital zircons from the Tintic formation show a wide range of igneous and metamorphic/fluid alteration textures. Many (Fig. 5a,b) contain internal zones with apparent oscillatory zoning while others (Fig. 5a,c,d) show clear metamorphic rims along with wispy internal disturbance textures

https://doi.org/10.5194/gchron-2024-27
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(Corfu, 2003). While the full dataset contains a wide range of U-Pb isotopic discordance (Fig. 6), individual grains can often display a wide range of internal age and chemical variability (Figs. 5,6).

Zircons from this sample show a range of $^{207}Pb/^{206}Pb$ ages between 1 Ga and 1.8 Ga, and a wide range in $^{206}Pb/^{238}U$ ages (Figs. 5,6), leading to a large spread in the associated discordance. In typical detrital zircon work, where filtering for concordance is normal (Gehrels, 2014), the vast majority of these analyses would be filtered out and not considered further. The U-Pb data were used as inputs into the updated version of the discordance modeling algorithm of Reimink et al. (2016). The results of modeling are shown in Fig. 7. As discussed previously, the discordance modeling produces a 'sum likelihood' value across a range of lower intercept ages, in this case from 0 to 50 Ma. Note that the lower intercept range is independent of the model outputs as the data reduction is conducted geometrically. The most likely lower intercept age is definitively greater than 0 Ma, as the model is capable of modeling future ages and likelihood declines rapidly prior to 0 Ma. The peak in likelihood is ~23 Ma, and sensitivity tests (Section 3.2) show that the best fit age is 22-25 Ma.

https://doi.org/10.5194/gchron-2024-27
Preprint. Discussion started: 28 October 2024

3.2 Sensitivity Analysis

In order to test the sensitivity of the results shown in Fig. 7 to individual data points or groups of data points and conduct uncertainty analysis, we conducted a bootstrapped resampled modeling routine. The full Tintic Formation dataset was resampled with a pick-and-replace method to create 1000 synthetic datasets that contained the same number of data points as the original dataset (407 analyses). Each of these synthetic datasets was put through the discordance dating method and summed likelihood lower intercept ages were calculated. The maximum summed likelihood values and the ages of those maximum values were aggregated for each synthetic dataset. Figure 6B shows the distribution of the 1000 resampled discordance models, the majority of which have lower intercept peaks that cluster between 18-28 Ma. These ages are centered on the youngest ages documented by Stearns et al. (2020) from endoskarn titanites with ages down to 23 Ma which have been found in the Alta Stock metamorphic halo. Our data show that discordance induced by metamorphic resetting and/or fluid induced Pb-loss at this time affected a large portion of detrital zircons in the Tintic formation and validates our theoretical approach to discordance dating of disturbances in detrital zircons.

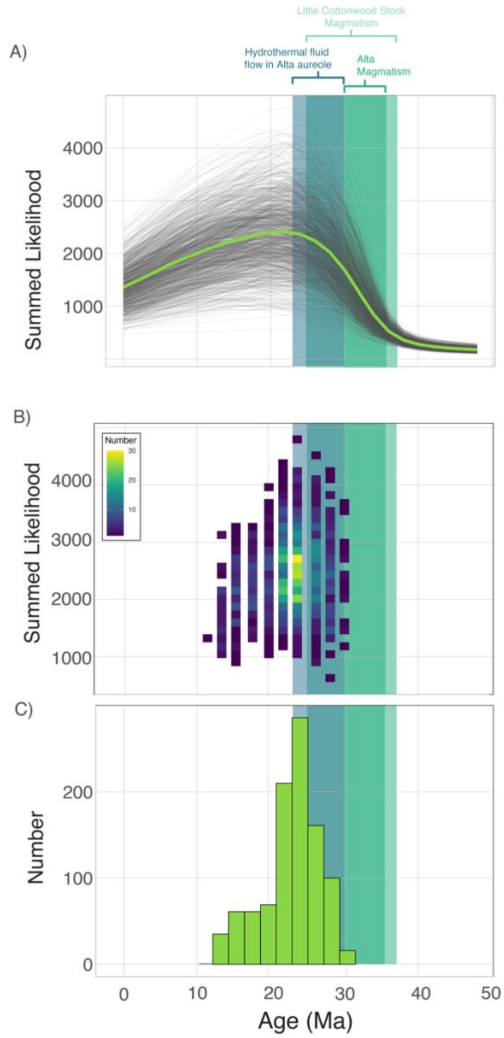

Figure 7: Outputs from discordance dating of Tintic formation zircons, and bootstrapped resampling efforts. A shows the summed likelihood lower intercept results of discordance dating. B shows the age and maximum sum likelihood value for each maximum value calculated from the curves shown in A. C shows a histogram of the peak positions in Ma.

Non-radiogenic Pb, termed 'common lead', can be found in meaningful concentrations in zircon, particularly metamorphic or otherwise perturbed zircon crystal lattices (Andersen, 2002; Schoene, 2014). The correction of this common Pb is necessary for accurate and precise geochronology, and several algorithms can be applied to remove the effect of common Pb from the U-Pb age calculations. The Tintic formation detrital zircon analyses do contain some common Pb, with higher concentrations present in a fraction of the more discordant analyses. To test if common Pb corrections influence our discordance dating methodology, we analyzed the Tintic formation zircons after two different common Pb correction types, in addition to the uncorrected data shown in Fig. 7 (green line in A). These results are shown in Figure 8. First, we apply various common Pb correction methods to subtract the contribution of 'common Pb' to the ^{206}Pb and ^{207}Pb signals. One common method (e.g., Schoene, 2014) is to use

https://doi.org/10.5194/gchron-2024-27
Preprint. Discussion started: 28 October 2024

the ^{204}Pb signal as an indication of the amount of common Pb, assume a Pb isotope composition using the Stacey-Kramers (Stacey and Kramers, 1975) global Pb-isotope evolution model, and subtract this common ^{206,207}Pb from the presumably radiogenic portion of the Pb. Another method involves the iterative solution to a series of equations assuming that the U/Th has not been disturbed and any time of Pb-loss is known (Andersen, 2002) – the latter assumption makes the method inappropriate for use with highly discordant data where the age of isotopic disturbance is unknown, data similar to the Tintic data evaluated here. Nevertheless, we show that there is little difference between the outputs of our discordance dating model on U-Pb data corrected using different common Pb calculations (Fig. 8), suggesting that the discordance dating lower intercept age is robust from the influence of common Pb, at least for the Tintic Formation zircon dataset evaluated here.

3.3 Causes of Discordance

The theoretical underpinnings of the discordance dating approach outlined here do not require any specific process to generate discordance in detrital zircon U-Pb data. As discussed previously, reliably isolating a discordance-inducing process requires additional in situ measurements (e.g., Raman mapping, e.g., Nasdala et al., 1998) that is outside the scope of the present manuscript.

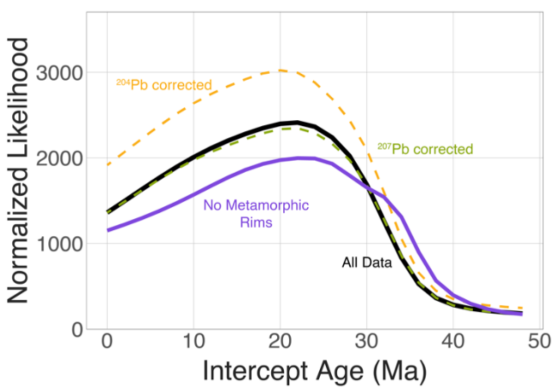

Figure 8: Plot showing the summed lower likelihood for Sample 2 U-Pb data with various common-Pb corrections applied. The black curves shows the base data with no common Pb correction. The orange curve shows the same data with a ^{204}Pb and Stacey-Kramers common Pb correction applied. The green curve shows the ^{207}Pb or Anderson correction applied to the same data. The purple line shows the lower intercept result for data that excludes all analyses that included a metamorphic rim growth feature. There is little change in the peak position across these various datasets, indicating that common Pb is unlikely to be affecting our results.

However, here we discuss our dataset in light of the current understanding of discordance and outline possible avenues forward. Of the range of viable discordance mechanisms outlined above, we focus on two categories: 1) dynamic metamorphic recrystallization or overgrowth (Hoskin, 2003; Hoskin and Black, 2002; Schoene, 2014) and 2) fluid-mediated without significant recrystallization (Geisler et al., 2002; Nasdala et al., 2010). These two categories of processes likely have many shared characteristics, such as the ‘dissolution-recrystallization’ process whereby hydrous fluids preferentially infiltrate decay-damaged portions of the zircon lattice and initiate structural annealing (Geisler et al., 2007). Such altered and annealed domains can contain micro-inclusions of other mineral phases such as thorite, xenotime, and uraninites, among others.

To distinguish between fluid-mediated Pb-leaching vs. recrystallization of zircon domains, we examined trace element data collected on the same zircon analyses spots via LASS measurements. If discordance in the Tintic zircon population was caused by metamorphic overprinting or recrystallization, the most discordant zircon analyses would be expected to have low Th/U typical of metamorphic zircon growth zones (Hoskin, 2003).

https://doi.org/10.5194/gchron-2024-27
Preprint. Discussion started: 28 October 2024

The Tintic zircons analyzed here show distinct trends between higher U concentrations and increased discordance, and correspondingly lower Th/U (Fig. 9). More discordant analyses also have higher Th, higher Al, and among the most discordant analyses occasionally higher ^{204}Pb (Figs. 5,9). The steady increase in U and Th concentrations with increasing discordance could be generated in two distinct ways. First, metamorphic zircon can contain higher U and Th concentrations than typical igneous zircons (e.g., Garber et al., 2020). So, increasing U+Th concentrations could be an indication of increasing metamorphic zircon growth in particular analytical volumes. This hypothesis is corroborated by an average decrease in Th/U with increasing discordance, typically used as a monitor for metamorphic zircon growth (Hoskin, 2003). This might suggest that discordant Tintic zircon domains were sites of preferential nucleation for metamorphic overgrowths.

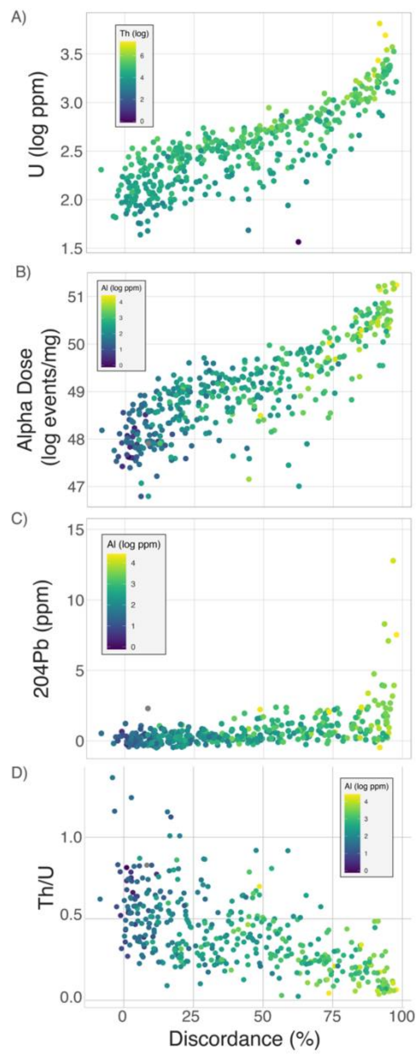

Figure 9: Zircon trace element data plotted as a function of discordance in the U-Pb system. Note that ^{204}Pb is frequently at negligible concentrations such that background corrections generate apparent negative values. Note that one data point with artificially negative ^{204}Pb concentrations is removed from the plot.

An alternative hypothesis based on fluid ingress into damaged zircon is, at this stage, equally viable. In this model, high U+Th igneous zircon domains led to more radiation damage from zircon crystallization until the ~30 Ma fluid alteration event. Indeed, discordance is highly correlated with the alpha dose of analytical volumes in the Tintic formation zircon population. At 30-25 Ma, reactive fluids may have preferentially infiltrated radiation-damaged (old, high U+Th) zircon regions, removed radiogenic Pb, introduced non-stoichiometric elements such as Al, and therefore induced discordance.

At the current time, definitively distinguishing between these two types of isotopic disturbance and resetting processes is not possible. However, differentiation could be done by, for instance, combining zircon U-Pb-TE data with Raman spectrometer analyses of altered domains that could quantify the crystallinity of the zircon lattice (Anderson et al., 2020; Nasdala et al., 2010; Resentini et al., 2020; Zhang et al., 2000) and help determine which of these two models, metamorphic recrystallization and/or fluid-induced Pb loss, was a dominant Pb-loss-inducing process in the Tintic zircon population. However, this would need to be accomplished prior to destructive analyses for U-Pb-TE via laser ablation.

An important consideration is what types of conditions are required to create the high degree of discordance that we have shown to be useful for geochronological studies. Though definitive

https://doi.org/10.5194/gchron-2024-27
Preprint. Discussion started: 28 October 2024

answers to this question will require more analyses from other locations with different styles of discordance, we can speculate using the Tintic dataset generated here. Zircon analyses from the Tintic formation in the Alta metamorphic aureole were qualitatively categorized by their visible morphology during SEM imaging in the following way: 1) the percentage of the spot location that included obvious metamorphic rim growth was determined and given a value of 0%, 25%, 50%, 75%, or 100%; 2) similarly, the percentage of the analytical spot location that included mottled and recrystallized zones was determined, and assigned the same discrete percentage classifications as the metamorphic rims; 3) a qualitative estimate of the amount of 'fractures' included in the analytical area was determined and the spots were assigned a value of 0 – no fractures, to 3 – many fractures. Examples of the zircons analyzed are shown in Figures 5 and 6, and the grain numbers with each category are given in Table 1. Note 34 analyses do not have classification systems as the SEM images were not of sufficient quality to determine the morphology.

Table 1: Classification table of analytical spot morphologies. Each spot is categorized according to three categories according to the CL imaging of spot locations. For all three categories, higher numbers mean more of each alteration morphology. Metamorphic rims are classed according to the percentage of each spot that included a metamorphic rim, from 0-100% rim. Fractures were ranked on a qualitative scale from 0-3 where 3 represented a highly fractured spot location. Mottled/Recrystallized was ranked similarly to metamorphic rim, on a scale from 0-100% according to the percentage of mottled or recrystallized domain in the spot location images.

	Metamorphic Rims (0-100)		**Fractures (0-3)**		**Mottled/Recrystallized (0-100)**	
Class	**Number**	**%**	**Number**	**%**	**Number**	**%**
0/0	222	54.5	15	3.7	258	63.4
25/1	37	9.1	69	17.0	8	2.0
50/2	29	7.1	123	30.2	16	3.9
75/3	48	11.8	166	40.8	8	2.0
100	37	9.1	-	-	83	20.4
NA	34	8.4	34	8.4	34	8.4

As shown in Figure 8 (purple line), running the discordance dating procedure on the 222 analyses that do not contain any metamorphic rim growth within their visible area produces very similar results to the discordance dating procedure run on the entire 407 analysis dataset. This suggests that discordance dating is possible on samples that have only internal alteration and recrystallization, and new, metamorphic zircon rim growth is not required to obtain accurate discordance dating ages. This is in contrast to data obtained on mixed xenocryst-new rim zircon analyses that can be used to determine difficult-to-obtain ages from thin igneous rim growth zones (Rasmussen et al., 2023).

4. Outlook and Future Directions:

Here we have showed that discordance dating may be used to date discordance-inducing events that affected detrital zircon populations. We have shown that this method provides several million-year age resolution on alteration events in rocks that experienced ~23 Ma fluid flow and metamorphism at temperatures that reached ~450°C. The high temperatures of metamorphism within the Tintic formation sample may lead to the perception that discordance dating is a tool that

https://doi.org/10.5194/gchron-2024-27
Preprint. Discussion started: 28 October 2024

is applicable to high-T metamorphic settings only. However, several pieces of data suggest that discordance dating may be an impactful method with wider applicability.

First, most zircon geochronologists pursue readily interpretable and therefore concordant data. Geochronologists tend to select spots targeting regions of high zircon quality and pick laser or ion probe analytical locations that are likely to retain a closed U-Pb system – a single metamorphic growth rim or a single domain of clearly igneous zircon. Additionally, what little discordant data may have been collected in laboratories around the world is commonly filtered based on a discordance threshold. Thus, there is no clear way to determine the general prevalence of discordant data in detrital zircon datasets. Additional analytical focus on discordant grain volumes may lead to additional insight into the value of discordant data for geochronological purposes.

Second, discordance dating will theoretically become more precise if discordant grains have older initial crystallization ages and the resetting event is relatively young. Due to the geometry of U-Pb isotope space, older grains experiencing more recent discordance-inducing geological events will provide a more precise estimate of lower intercept ages. However, though the Tintic formation contains grains with primary ages up to ~1.8 Ga, other more ancient grains would provide additional precision to any discordance dating analysis. The larger the age dispersion in detrital zircon crystallization ages, the more precision discordance dating would yield for Phanerozoic alteration events. Thus, a sediment that experienced less aggressive fluid flow or metamorphism, but that had older detrital zircon grains, may yield important lower intercept age information, with uncertainties on the order of a few million years.

Third, there is a growing body of evidence that discordance in zircon can be induced in a wide variety of low-temperature environments. Both experimental (Geisler et al., 2001; Pidgeon et al., 1966) and empirical (Geisler et al., 2002; Morris et al., 2015; Pidgeon et al., 2016; Zi et al., 2022) studies have documented large degrees, and sometimes near total, discordance at much lower temperatures (100-200 C) than the Tintic formation zircons analyzed in this work experienced. Thus, it is possible that many suites of detrital zircons experienced low-T hydrothermal fluid flow events that induced Pb-loss and/or recrystallization to such a degree that discordance dating could provide useful age information. This is particularly relevant as there are a limited number of geochronometers that are currently available to date reactive fluid flow events (brine migration, mineralizing fluid flow, low-T metamorphism, etc.) in sedimentary rocks– even imprecise age information is useful in such scenarios.

5. Conclusions:

We have documented a potential new tool for geochronologists to use to date in situ detrital zircon Pb loss events. We have shown the utility of this technique using extensive testing using synthetic datasets and ground-truthing by analyzing zircons within the well-studied Alta Stock metamorphic aureole. The discordance dating technique returns discordance ages of ~23 Ma, which is the expected age of fluid flow in this region. Our method may have significant applications to determining rates and absolute dates of diverse geologic phenomena; basin brine migration, mineralizing fluid flow, and low-grade burial metamorphism are just a few of the processes that may induce discordance in zircon analytical volumes such that it is amenable to discordance dating. Our preliminary data suggest that detailed in situ characterization and isotopic tools will help address fundamental questions on the nature of zircon U-Pb disturbance.

https://doi.org/10.5194/gchron-2024-27
Preprint. Discussion started: 28 October 2024

Acknowledgements:
This work was supported by Rudy L. Slingerland Early Career Professor of Geoscience funds awarded to JRR.

Data Availability:
The data reduction code and raw data used for discordance modeling is available here: https://github.com/jreimink-isotope-geochem/discordance-dating and at the following Zenodo DOI 10.5281/zenodo.13972610
and a public-facing easy-to-use Shiny app is available here:
https://discordance.geosc.psu.edu/discordance_app/

Competing Interests:
The authors declare that they have no conflict of interest.

Author Contributions:
JRR, JD, and MKL conceived the study. AJS carried out sample collection. RB, ES, AC, and JG separated zircons, collected U-Pb-TE data, and produced final results. JRR and JD carried out modeling and sensitivity testing. All authors contributed to final data interpretation and manuscript production.

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