



# Potential for constraining sequence stratigraphy and cycle stratigraphy with U–Pb dating of carbonates

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## ABSTRACT

Studies of sequence stratigraphy and cycle stratigraphy in carbonate formations increasingly improve our understanding of depositional systems and basin to global correlations. However, there is still a scarcity of dated sequences to determine the time length of sequences and cycles. The durations of sequences and cycles provide tests of the processes that produce them. Poor age resolution mostly stems from the lack of recognizable volcanic ash deposits in many sections. Through continuing advances in analytical techniques and approaches to sampling, the current state of U–Pb dating of carbonate sedimentary rocks provides opportunities to fill in age gaps. The approach should build on well-constrained 3-dimensional stratigraphic architectures and diagenetic stratigraphies.

Over the last 10 years there has been an explosion in the application of U–Pb dating of carbonates with the introduction of Laser Ablation (LA) ICPMS analyses. What these studies show is that measured carbonate ages are often younger than the age of deposition and in many cases, multiple ages are derived from individual samples, indicative of multiple events. Often these younger events can be tied to known tectonic activity or sea level changes that would have influenced hydrology, perhaps bringing in new reactive fluids to dissolve or replace some existing minerals and precipitate new minerals. U–Pb dating of carbonates offers unprecedented potential to work out the timing of deposition and diagenesis in carbonate sequences. As more samples are investigated, particularly in the context of field, petrographic, and geochemical constraints, our views on how to sample and the reliability of ages will be strengthened. Additionally, as more primary and secondary natural reference materials with different textures and mineralogy are made available, our ability to evaluate the reliability of LA ICPMS ages of unknowns will improve. While ages of U–Pb carbonate will likely never approach the precision of U–Pb zircon and Ar–Ar sanidine dating of tuffs, carbonates have the advantage of being abundant in space and time, often occurring where volcanic ash deposits are not recognized.

Here we review geochronology from Carboniferous–Permian cyclothems that have been shown in numerous studies to be driven by glacio-eustasy, presumably paced by Milankovitch cycles, and that can be understood in a sequence stratigraphic framework. We compare U–Pb carbonate ages with other radiometric ages and biostratigraphy to demonstrate the reliability of the carbonate ages and thus highlight potential. We show new Laser Ablation U–Pb Carbonate data for a particularly well-studied paleosol carbonate with outstanding U–Pb systematics and compare with published isotope dilution ages, particularly focusing on the power of the image-based approach to carbonate dating advanced by Drost et al. (2018). Finally, we compare results between U–Pb zircon dating and U–Pb carbonate dating of cyclothems with Bayesian modeling and conclude that numerous lower precision dates throughout a stratigraphic section provide age constraints that can be similar in precision to a few highly precise ages, depending on the stratigraphic distribution throughout the section.

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## 1. Introduction

The questions we are asking of the rock record create a great demand for improved time resolution. This demand is highlighted by the National Academies 'A Vision for NSF Earth Sciences 2020-2030: Earth in Time' (2020), which describes a need for better temporal constraints to test geologic models. This is especially true in the carbonate rock record, and for sequence stratigraphic architectures. Sequence stratigraphy and cycle stratigraphy in carbonate formations increasingly reveal information about temporal and spatial changes in depositional environments, and push our understanding of potential drivers, such as eustatic sea level. However, there is still a scarcity of geochronological constraints to test cycle durations and provide constraints on rates of sedimentation. Through continuing advances in analytical techniques and approaches to sampling, the current state of U—Pb dating of carbonates makes the goal of widespread absolute dating of carbonate stratigraphy more possible than ever before. These advances occur on the back of decades of U—Pb developments and well over a century of developing concepts of carbonate sequence stratigraphy (before it was called that). We briefly review this history to provide context for current advances and suggest directions for future applications of carbonate geochronology to sequence stratigraphy.

A significant portion of shallow carbonate rocks, if not all, preserve rhythms of deposition recorded by 3-dimensional facies distributions. Superposition, cross cutting relationships and stratigraphic changes in vertical thicknesses and lateral facies distributions define cycles of many scales commonly with multiple hierarchies. Such details in Late Paleozoic cyclothems have been recognized and studied for over a century (e.g., Fielding, 2021; Montañez, 2022; Wanless and Shepard, 1936). During the 1950s through 1970s with improved understanding of carbonate facies, cycles and sequences were increasingly recognized in most platform carbonates, as exemplified in the syntheses of Wilson (1975). At this time, it was realized that the facies distribution and extent of carbonates are sensitive to sea level and follow the "principle of fast but rapid deposition" such that carbonate strata are likely dominated by periods of non-deposition (Wilson, 1975).

The advent of seismic sequence stratigraphy fueled the use of onlap and offlap of strata to provide a record of regional sea level change (Vail et al., 1977). By comparing basins across the globe it appears possible to pull out the eustatic signal (e.g. Haq and Schutter, 2008). Using fusulinid biostratigraphy and onlap-offlap sequences, Ross and Ross (1985) argued that Late Paleozoic 1–5 Ma sequences responded to eustatic changes in sea level and were 'synchronous and world-wide'.

After refinements by Van Wagoner et al. (1988), use of sequences and terminology to describe their components became more widespread. Sequence stratigraphic analysis on carbonate rocks reached a renewed level that continues to the present. During this time, two of many important points with respect to this paper became more recognized. 1) The different scales of stratigraphic packaging or architecture were defined by 3-dimensional cycles and that single vertical sections alone are insufficient to define the cyclicity (e.g. Kerans and Tinker, 1997). 2) The packaging of the cycles differs during icehouse and greenhouse times (Read et al., 1995; and see Montañez, 2022; Fig. 4 for current view).

By 2000, our level of understanding of hierarchical cycles in carbonates was becoming quite sophisticated. This understanding was dependent on sea-level curves and proxies which have become increasingly better understood. Correlations, biostratigraphy, chemostratigraphy and sea level trends were and are determined from carbonate strata and carbonate minerals. However, most sequences were undated so that scales of cycles and global correlations were untested by geochronology. The Carboniferous-Permian boundary as an excellent example that is pertinent to this paper. Harland et al. (1990) Geological Timescale reported the Carboniferous-Permian boundary at  $290 \pm 20$  Ma ( $2\sigma$ ), an uncertainty that precludes answering many questions we ask of the stratigraphic record, let alone of any meaningful time

analyses.

Prior to the mid 1980's radiometric age dates for carbonate strata older than Pleistocene were on minerals in ashes, volcanic layers, and intrusions. The earliest work on dating carbonates used Pb—Pb to date Archean stromatolites (Moorbath et al., 1987). While the Pb—Pb was later shown to likely result from Pb mineralization and was thus not a primary age (Sumner and Bowring, 1996), this spurred the first U—Pb carbonate race, as a number of papers using U—Pb followed and showed the great potential for providing improved time constraints (summarized in Rasbury and Cole, 2009). This earlier work used isotope dilution (ID) which is time consuming and lacks opportunities for prescreening for favorable samples, which slowed advances. Determining which samples might work was improved somewhat with imaging techniques like phosphor imaging (Cole et al., 2003), but high uranium is not the only key to success and this imaging did not address the Pb content.

LA ICPMS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) analyses of carbonates has greatly expanded the potential for identifying datable carbonates. This technique, established by Randy Parrish at NIGL (British Geological Survey NERC Isotope Geosciences Laboratory) set the stage for a new revolution in U—Pb dating of carbonates. The first analysis using LA ICPMS to date carbonates was published in 2014 (Li et al., 2014) in a study aimed at constraining Jurassic stratigraphy. In this case the biostratigraphy was good enough to recognize that the dated cements were too young to represent the time of deposition. However, the study highlighted the great potential for LA ICPMS to date carbonates. Since that first contribution, details of data reduction and reference materials are still being ironed out, but numerous labs are participating in the effort. Laser Ablation ICPMS dating of carbonates was highlighted during the 2018 Goldschmidt Conference, in a workshop on LACarb, which we adopt as a short title for laser ablation U—Pb dating of carbonates here. The LACarb website maintains an extensive bibliography of LACarb work since 2014 (<https://la-carb.com>), and welcomes researchers to join this group. Much of the recent application of LACarb has been on carbonate mineral filling fractures, in efforts related to unraveling later fluid flow and tectonic events, recently summarized by Roberts and Holdsworth (2022).

Initial LACarb techniques did not solve many of the issues of sample selection needed for widespread application to carbonate stratigraphy. Carbonates are soluble in many solutions and subject to alteration through time. Some of these features are too subtle to be easily recognized with conventional petrography. Many of these issues are solved with an exciting development in LACarb using an image based approach to pooling pixels (Drost et al., 2018) and a follow up of this using robust regression of all of the data (Hoareau et al., 2021; Rochín-Bañaga et al., 2021), which we will refer to as the Drost method. This approach is particularly appealing for labs using a quadrupole mass spectrometer because pixels can be selected by criteria such as element concentrations or ratios. Often carbonates have distinctive compositions (high Mg or low Mg calcite, dolomite etc.) and trace element compositions that can be understood in the framework of the hydrological system(s) that formed them. For carbonates, which are vulnerable to diagenetic change, this ability to visualize element maps in the context of petrography offers a huge advance not only for dating, but also for deciphering more about the fluids that formed and/or altered them.

## 2. Environmental controls on U and Pb in carbonates

### 2.1. Syn-sedimentary carbonates

Syn-depositional carbonates form in marine, terrestrial and transitional environments. A major bottleneck for U—Pb dating is recognizing conditions that produce relatively high and variable U—Pb ratios (Rasbury and Cole, 2009). While early work focused more on the U content of carbonates (Amiel et al., 1973; Chung and Swart, 1990; Cole et al., 2003, 2004; Gvirtzman et al., 1973; Haglund et al., 1969; Hoff

et al., 1995; Lahoud et al., 1966; Rasbury et al., 2000; Schroeder et al., 1970), it is equally important to understand Pb concentrations (and thus the U/Pb ratios) for U–Pb dating (Rasbury et al., 2021; Rasbury and Cole, 2009; Woodhead et al., 2006). Understanding the geochemistry of the fluids that are responsible for carbonate precipitation is key to predicting what types of carbonates hold potential for U–Pb dating. Though, using existing chemical constraints published on carbonates to assess potential samples amenable for dating is complicated by the fact that U is not typically reported in carbonates except for dating (we want to change that) and unsuccessful attempts at dating commonly go unreported. Below we provide ideas on geochemical characterization of carbonates sorted by depositional environment, which can serve as a foundation from which to build a more comprehensive database of environmental conditions that most typically produce carbonates with favorable U–Pb ratios.

Rasbury and Cole (2009) reviewed U–Pb dating of carbonates in the context of the hydrologic realms that these carbonates were formed in. At about that time, U–Pb dating of speleothems by Multi-Collector ICPMS (MC-ICPMS) was gaining momentum (Woodhead et al., 2006, 2012; Woodhead and Pickering, 2012). Woodhead et al. (2006) showed that screening approaches that had been used for U-series dating were also helpful for identifying favorable samples for U–Pb dating. This is because Pb and Th are both mostly insoluble in surface fluids. Even with this predictive approach, finding samples with favorable U/Pb can be difficult, but laser ablation methods offer an exciting avenue to not only date rocks, but to learn fundamental details of the geochemistry in the context of these ages. As more samples are analyzed in the context of detailed stratigraphy, and with an eye towards how these samples reflect the fluids that formed them, important patterns will emerge that will further refine approaches to carbonate dating.

## 2.2. Marine carbonates

Marine carbonate components have evolved through time due to biological evolution and evolution of ocean chemistry. This includes the dominant mineralogy of skeletal material at any one time (Pomar and Hallock, 2008; Stanley and Hardie, 1998). Marine cements and skeletal calcium carbonates include aragonite, low-Mg calcite, and high-Mg calcite. Carbonates in modern marine environments are dominantly aragonite and high-Mg calcite, low Mg calcite is only dominate in deep cold waters. The major mineralogy plays a role in U incorporation into the carbonates. Aragonite does not exclude U, while calcite does (Reeder et al., 2000).

It has been shown that the major ion composition of seawater has fluctuated through the Phanerozoic (Dickson, 2002; Hardie, 1996; Horita et al., 2002; Lowenstein, 2001). Changes in the Mg/Ca of seawater appears to have dictated whether the favored calcium carbonate was aragonite (high Mg/Ca seawater) or calcite (low Mg/Ca seawater) (Hardie, 1996). Importantly, these major cycles appear to correspond to icehouse (high Mg/Ca) and greenhouse (low Mg/Ca) periods on Earth. Certainly the correspondence between times of aragonite seas producing MgSO<sub>4</sub> evaporites, versus times of calcite seas producing KCl evaporites in bittern salts strongly implicates secular changes in major ions in seawater, rather than some other control such as atmospheric pCO<sub>2</sub> (Hardie, 1996). Hardie (1996) used a simple assumption that seawater is a two-component mix between river waters and fluids emerging at the Mid Ocean Ridge (MOR) after interacting with and altering oceanic crust. Small changes in the seawater flux through the MOR can predict the fluctuating Mg/Ca ratio (Hardie, 1996), but additional constraints must be imposed to account for K, which does not appear to change through time (Demichio et al., 2005). Other studies have downplayed the importance of MOR circulation and find that during times of high sea level more carbonates are dolomitized, driving sea water to lower Mg concentrations, and more evaporites form on the shelves, driving sea water to lower sulfate concentrations (Holland et al., 1996). It is also true that as seawater changes, so do the

reactions along the pathway in the MOR (Antonelli et al., 2017) and on the shelf. Models for secular changes in seawater will be improved, but importantly, work from Cenozoic aragonitic corals (Denniston et al., 2008; Getty et al., 2001; Gothmann et al., 2019) shows an increase in U through the Cenozoic as the Earth moved from calcite seas into aragonite seas (Fig. 1). While part of this increase could simply result from decreasing Ca concentrations, this cannot account for all of the change (Gothmann et al., 2019).

Marine cements from the Carboniferous-Permian have U concentrations comparable to the Neogene, consistent with U reflecting secular change (Fig. 1). We suggest that times of aragonite seas, like today, the Late Paleozoic, and the Neoproterozoic, may have elevated U in carbonates, and conversely, times of calcite seas likely have lower U in carbonates because a main control is the U/Ca ratio of the parent fluid. The major mineralogy also plays a role in U incorporation into the carbonates (Reeder et al., 2000). This makes the shift to more elevated U concentrations into the Neogene aragonite seas even more significant as aragonite formation would sequester more U and would drive a downward trend. Interestingly, Sr also shows a trend with these major cycles (Steuber and Veizer, 2002) that is opposite that of U. Trace elements are powerful proxies for process because they do not control the system, the simply respond to it. As more detail becomes available for U in marine carbonates, we expect that the drivers will be revealed.

Aragonite is metastable and will dissolve or be replaced by low Mg calcite by dissolution and re-precipitation processes. Understanding the details, especially the timing, of these changes is key to identifying syn-sedimentary carbonates that can be dated by U–Pb to provide the age of deposition. Rasbury et al. (2004) showed that marine cements from the Late Carboniferous, which were aragonite altered to calcite, formed soon after deposition and preserved elevated U concentrations despite neomorphic conversion to calcite. Similar neomorphosed marine cements from the Permian Reef Complex of West Texas and New Mexico provided the WC-1 reference material for LACarb dating (Roberts et al., 2017).

## 2.3. Terrestrial carbonates

Carbonates formed in terrestrial environments are far less predictable than marine environments because water chemistry varies widely depending on the regional geology and hydrology. Speleothem deposits have been a target for U-series dating and a summary of the prospects for U–Pb dating can be found in review papers such as Woodhead and Pickering (2012). Speleothems form from meteoric diagenesis, and this has been well covered elsewhere (e.g. Woodhead et al., 2006). Basically, the layering of speleothems and the ability to date them provides important details of the climate at the time of formation, but they often form much later than the time of deposition of the rocks they occur within. Calcrete (caliche) is another meteoric product that forms at subaerial exposure. This too can be much later than the time of actual deposition, and age uncertainties could be large due to the long-term exposure. For example Hoff et al. (1995) analyzed dolomites associated with subaerial diagenesis from the Pre Upper Permian Unconformity (PUPU) of the Wahoo Fm in the Brooks Range, Alaska, and obtained an age of  $267 \pm 31$  Ma ( $2\sigma$ ). This age is consistent with the unconformity it formed on, but with an uncertainty that was as large as the expected duration of the exposure (30–40 m.y.). Winter and Johnson (1995) also dated dolomite associated with the major sequence boundary of the Sauk and Tippecanoe sequences in Wisconsin, USA and obtained an age of  $504 \pm 14$  Ma ( $2\sigma$ ), entirely consistent with the biostratigraphic framework. These studies showed that U can be concentrated at sequence boundaries and set the stage for examining marine and terrestrial sequences with 4th (<0.5 m.y.) and 5th (<0.1 m.y.) order sequence boundaries (Brigaud et al., 2021; Kurumada et al., 2020; Rasbury et al., 1997, 1998, 2000, 2006; Wang et al., 1998).

Lakes may also be sites of prominent carbonate deposits, and the position and stacking patterns of lacustrine facies can be used to show

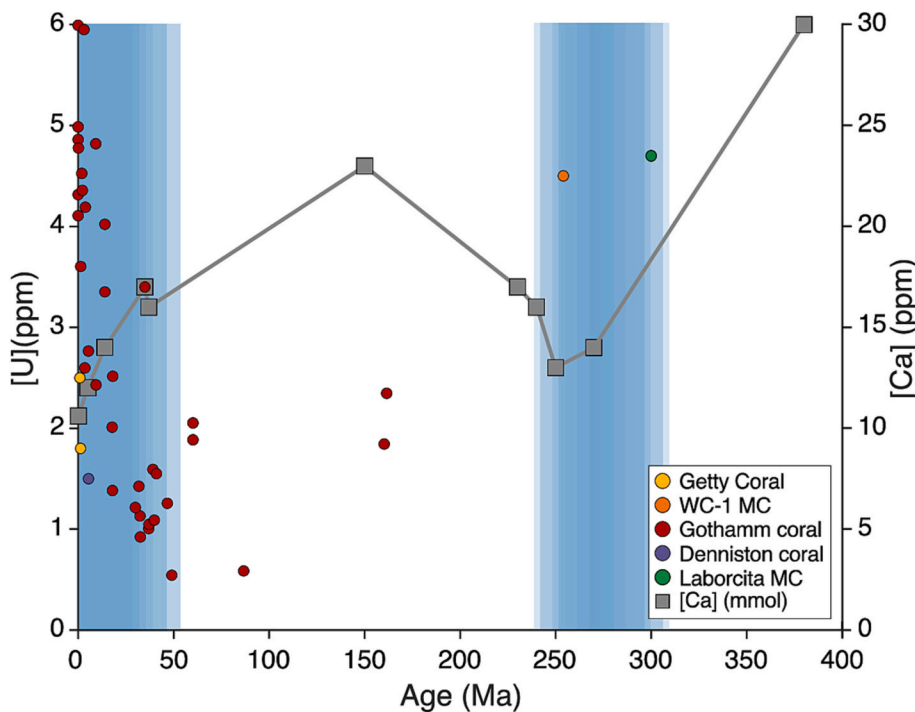


Fig. 1. U concentrations in corals and marine cements relative to time of aragonitic seas. Data are from Laborcita fAMC (former aragonite marine cement) from Rasbury et al. (2004), and WC-1 fAMC from Roberts et al. (2017). Coral aragonite data are from Getty et al. (2001), Denniston et al. (2008) and Gothmann et al. (2019). Blue shaded areas are the approximate time intervals of aragonite seas. The gradient in shading is intended to reflect the temporal uncertainties and gradation of these boundaries. Grey squares and curve represent Ca concentration data from fluid inclusions in evaporites (Horita et al. (2002)). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

changes in lake level that allows geologists to consider hydrological changes in the context of climate and tectonics (Carroll and Bohacs, 1999). Lacustrine carbonates from a variety of settings have been dated by U—Pb (Cole et al., 2005; Lawson et al., 2022; Montano et al., 2021, 2022; Piccione et al., 2022). A focus on the lake chemistry and U incorporation in carbonates is sorely needed for better predictions of lacustrine samples amenable for U—Pb. This is especially true given that some lacustrine carbonates do not have favorable U—Pb ratios and any attempts to date them are likely to not have been published.

A recent contribution from Montano et al. (2022) studied Late Cretaceous to Paleogene carbonate bearing lacustrine sequences in Argentina and showed that age models based on U—Pb zircon dating (LA ICPMS dating of detrital zircons to determine the Maximum Depositional Age (MDA)) compare quite favorably with those based on U—Pb dating of carbonates. Using careful petrography and an understanding of the carbonate facies that were being sampled, these authors considered all of the data obtained from each horizon using the MSWD of the population of isochron ages from each horizon to determine if the data met the criteria to be included. This work elegantly demonstrates the power of using LACarb for dating terrestrial sedimentary sequences and sets a bar that any studies that seek to improve stratigraphic time resolution should meet or exceed.

#### 2.4. Transitional environments

Much of the alteration of marine carbonates occurs in transitional environments (e.g. Heckel, 1983). When sea level is rising or falling, recently deposited sediments are subjected to different fluids, which are not necessarily in equilibrium with the marine deposits. The mixing zone between marine and freshwater, as well as the boundaries between the marine vadose and phreatic zones, move with transgressing and regressing seas (or lakes). Details of diagenesis in the context of depositional packages are recorded in cements and dissolution events, and all of these changes can be considered in the framework of sequence stratigraphy (Morad and Ketzer, 2013). Carbonates produced in this context that can be dated with U—Pb will improve our understanding of the boundaries as well as improve age resolution of the sections they occur within (Table 1; at the end of the document).

### 3. Application of carbonate U—Pb constraints in sequence stratigraphy

#### 3.1. Sequence stratigraphic boundaries

Sequence stratigraphy provides a framework from which to think about associated facies in the context of base level change, and the types of fluids (meteoric, seawater, etc.) that might have interacted with the deposits to alter depositional minerals and form new minerals throughout the evolution of a basin. Sequence boundaries are the fundamental surfaces that bracket systems tracts (transgressive, highstand, regressive, etc) and the details of these tracts provide insight into changes in accommodation space and/or sediment supply. Often, the sequence order can be defined, such as 3rd, 4th and 5th order cycles. Diagenesis such as hardground formation in starved deep-water transgressive systems tracts, or meteoric diagenesis (e.g. karst) and soil formation during subaerial exposure at low stands, can be profound. If the sequences are 4th (<0.5 m.y.) or 5th order (<0.1 m.y.) cycles, the duration of this alteration is typically smaller than the reasonably expected uncertainties in the ages of diagenetic minerals that formed as the surface was active (Brigaud et al., 2021; Rasbury et al., 1997). In detail, textures that appear to be early diagenesis can give ages that are significantly younger than the age of deposition (Brigaud et al., 2021; Israelson et al., 1996; Li et al., 2014; Montano et al., 2022; Wang et al., 1998). Thus, in concert with field and petrographic observations, U—Pb dating of carbonates will reveal details of diagenetic fabrics that will improve how we understand the systems that created or altered them (Table 1).

#### 3.2. An example: Carboniferous-Permian cyclothems

As originally defined in the Illinois Basin of North America, cyclothems represent high-amplitude and high-frequency changes in sea level that resulted in marine to non-marine packages with evidence for subaerial exposure (Wanless and Shepard, 1936). Wanless and Shepard (1936) made a case for the correlation of cyclothems globally and suggested that improved paleontology and other age constraints could help to refine these correlations. Following that work numerous studies have



**Table 1**

Summary of major diagenetic processes due to marine sequence stratigraphic controls with predicted carbonate cements and potential for U—Pb dating. Table modified from (Morad and Ketzer, 2013).

Processes and Products	Climate/Setting	Predicted U-Pb	Potential for U—Pb dating	Reference/source
<b>Sequence Boundaries</b>				
Dissolution and karstification	Humid/subaerial	May provide a fluid with high U high if aragonite or low if calcite	good	
Phreatic meteoric cementation	Subaerial	Depends on a source of U.	good	(Chung and Swart, 1990)
Dedolomite	Subaerial	If the original dolomite was 'hot' it is possible the carbonate formed from it will have elevated U. However, the Fe oxides that often accompany this transformation have a high affinity for U and may make it unavailable for the carbonate.	unknown but promising	
Pedogenesis and calcrete formation	Subaerial	Depends on a source of U but several examples show potential for calcite and dolomite at subaerial exposure surfaces. U-series work on pedogenic carbonate on alluvial gravels has high potential (Blisniuk et al., 2012; Blisniuk and Sharp, 2003; Fletcher et al., 2010, 2011; Gold et al., 2011, 2015; Rockwell et al., 2019; Sharp et al., 2003). Carnotite found in association with calcretes may sequester U so that the calcite has unfavorable U—Pb (Hall et al., 2019; Langford, 1974).	good	(Hoff et al., 1995; Rasbury et al., 1998, 2000, 2006; Wang et al., 1998; Winter and Johnson, 1995).
Dolomitization from evaporation	Coastal	Evaporitic fluids are enriched in Mg and U, evaporative dolomites are frequently 'hot'.	good	(Luczaj and Goldstein, 2000).
Dolomitization from mixing fluids	Coastal	Seawater freshwater mixing zones can produce dolomite with	good	(Rasbury et al., unpublished; Florida aquifer)

**Table 1 (continued)**

Processes and Products	Climate/Setting	Predicted U-Pb	Potential for U—Pb dating	Reference/source
<b>Parasequence boundaries, transgressive surfaces, maximum flooding surfaces</b>				
Dolomitization	Marine	reasonably high U and U—Pb. It is not clear that dolomite should have a stronger preference for U than calcite (which is very low). However, there are numerous examples of dolomite with elevated U and U—Pb and more work is needed to understand this.	good	(Elisha et al., 2020).
Hardgrounds and firmgrounds	Marine	Carbonates that form on these types of surfaces appear to be very promising for U—Pb dating	good	(Brigaud et al., 2021).
Isopachous Mg-calcite and aragonite cements	Marine	These carbonates have a higher affinity for U than low-Mg calcite and depending on how the minerals are transformed or dissolved this is a potential source of U to newly formed calcite.	good	(Chung and Swart, 1990)
Dolomite and calcite cements	Mixed marine-meteoric	Seawater freshwater mixing zones can produce dolomite with reasonably high U and U-Pb	good	(Rasbury et al., unpublished; Florida aquifer)
Dissolution related to coals on TS and in early TST	Mixed marine-meteoric	If the minerals that are being dissolved have elevated U, this potentially provides U for the next generation of carbonate cements.	unknown	
<b>Highstand systems tracts</b>				
Mg-calcite and aragonite cements	Shallow marine	These carbonates have a higher affinity for U than low-Mg calcite and depending on how the minerals are transformed or dissolved this is a potential source of U to newly formed calcite.	good	(Chung and Swart, 1990)
Dolomite and calcite cements	Mixed marine-meteoric	Dolomite and calcite are relatively stable carbonates. The U—Pb will	unknown	

(continued on next page)

Table 1 (continued)

Processes and Products	Climate/Setting	Predicted U-Pb	Potential for U—Pb dating	Reference/source
Pressure dissolution	Marine	depend on source of U and details of the Kd (for dolomite). This may provide a source of U for later carbonate cements.	unknown	
Mg-calcite and aragonite cements	Deep marine	This may provide a source of U for later carbonate cements.	unknown	
Meteoric dissolution	Meteoric or mixed	This may provide a source of U for later carbonate cements.	good	Chung and Swart (1990)
<b>Transgressive systems tracts</b> Mg-calcite and aragonite	Marine	These minerals are metastable but their formation provides a source of U for future carbonate cements.	good	Chung and Swart (1990); Rasbury et al. (2000)
Dolomitization (seawater)	Marine	It appears that dolomite may have a higher Kd for U than calcite. More work is needed on dolomite cements.	unknown but promising	(Elisha et al., 2020)

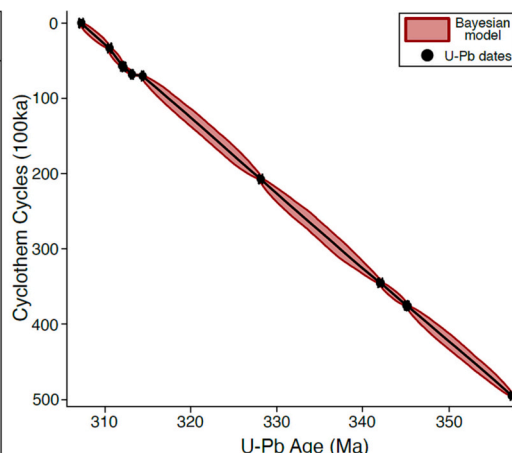
examined cyclothem records across basins and in agreement with Wanless and Shepard (1936) have shown that they represent high-amplitude (>100 m), likely glacio-eustatic changes in sea level. The magnitude and beat of these cycles offers a high resolution record of the waxing and waning of southern hemisphere glaciers (Crowell, 1978; Heckel, 2008). Paleontological studies allow refined cyclothem correlations globally (Davydov et al., 2010; Ross and Ross, 1985), and age constraints from ashes and paleosols have refined the initiation of glaciation, global correlations and cycle durations (Davydov et al., 2010; Eros et al., 2012; Pointon et al., 2021; Rasbury et al., 1998). Within that framework, the initiation of glaciation in the Carboniferous may be defined by the earliest recognized cyclothem (Bishop et al., 2009; Fielding and Frank, 2015; Smith and Fred Read, 2000; Wright and Vanstone, 2001) near the end of the Lower Carboniferous (within the Viséan). The end of Late Paleozoic glaciation may be defined by the end of high-amplitude high-frequency cycles (Saller et al., 1999), which occurs in the Lower Permian (within the Leonardian). Fielding (2021) reviewed cyclothem records specifically in the context of sequence stratigraphy and detailed the cycle orders, providing a foundation for global correlation. The duration of cyclothem has been tested through radiometric age constraints (Davydov et al., 2010; Eros et al., 2012; Pointon et al., 2021; Rasbury et al., 1998; Saller et al., 1999). It has long been recognized that Late Paleozoic Ice Age (LPIA) glacial centers shifted across the Gondwanan continents as this mega-continent moved across the south pole (Crowell, 1978; Wanless and Shepard, 1936). More recent studies provide radiometric dates for these glacial and glacio-marine deposits, confirming and refining this understanding of a dynamic system that shifted through time, rather than one large ice sheet that lasted from the beginning of the icehouse to the end (Dietrich et al., 2021; Griffis et al., 2019; Gulbranson et al., 2010). Climate modeling for the LPIA suggests that eccentricity paced climate (Horton et al., 2012). A detailed paleosol proxy record for the LPIA shows swings in pCO<sub>2</sub> that correspond to the glacial-interglacial record from the southern hemisphere (Montañez et al.,

2007). The cyclothem record supports a dominant eccentricity control on LPIA climate (Montañez, 2022).

The character of cyclothem records reflects the latitude, climate and tectonic environment of deposition (Wanless and Shepard, 1936). In the Southwest United States cyclothem records are mixed carbonate siliciclastic packages (Wilson, 1967). During sea level highstands, the basin was starved, carbonates formed in the shelf area, and siliciclastics were deposited in near shore to terrestrial environments (Wilson, 1967). During sea level lowstands, the marine carbonates were exposed to meteoric diagenesis and siliciclastics were transported across the exposed shelf into the basin (Wilson, 1967). Wilson (1967) termed this cyclical-reciprocal sedimentation. Paleosol carbonates formed atop marine carbonates after high-amplitude sea level drops (Goldstein, 1988; Saller et al., 1994). Goldstein (1991) used cement stratigraphy and stable isotopes to demonstrate that meteoric diagenesis was confined to the exposed cycle in the Sacramento Mountains of New Mexico. He reasoned that this resulted from the permeability barrier at the base of the cycle, perhaps from the preceding subaerial exposure event. Saller et al. (1994) showed that porosity development in cyclothem strata was controlled by the duration of exposure. With long-term sea level rise, cycles experienced shorter durations of exposure and enhanced porosity, while with long term sea level drop, exposure was intensified, destroying porosity, cycles are shorter, and there are missed cycles (Saller et al., 1994, 1999).

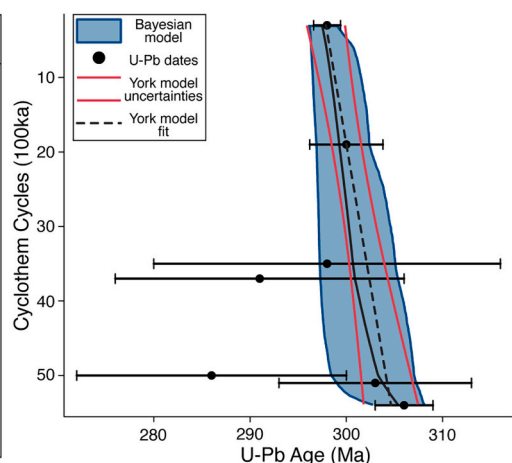
Building on this foundation, Rasbury et al. (1998, 2000, 1997) tested the potential for U—Pb dating of calcites produced during subaerial exposure (paleosols). Using the paleosol U—Pb ages in the context of biostratigraphy and cycle stratigraphy, Rasbury et al. (1998) estimated the age of the Carboniferous-Permian boundary to be  $301 \pm 2$  Ma (2 $\sigma$ ). At the time of that publication, the Harland et al. (1990) Geological Timescale had this boundary at  $290 \pm 20$  Ma (2 $\sigma$ ). Subsequently, Ramezani et al. (2007) presented high precision zircon ages from the type section in the Ural Mountains and estimated that boundary to be  $298.90 \pm 0.31/-0.15$  Ma (2 $\sigma$ ), impressively precise and entirely consistent with the U—Pb carbonate age estimate of that boundary. In addition to the paleosol ages, Rasbury et al. (2004) dated neomorphosed aragonite marine cements from the Laborcita Formation in the Sacramento Mountains of New Mexico and obtained an age of  $300 \pm 3.8$  Ma (2 $\sigma$ ). The algal mounds that these marine cements derived from, is approximately two high-frequency cycles before the Carboniferous-Permian boundary (Rasbury et al., 2004), and is thus entirely consistent with the Ramezani et al. (2007) age estimates for this biostratigraphic interval. Combined, these ages offer an opportunity to consider cycle durations and compare with high-precision dated records in the Donets Basin (Davydov et al., 2010). Davydov et al. (2010) dated 12 ashes and tonsteins in the Donets Basin. Based on these ages, they estimate the duration of cyclothem to have been  $83 \pm 24$  ky (Davydov et al., 2010), consistent with the estimate from the southwest United States of  $143 \pm 64$  ky (Rasbury et al., 1998). With their longer term record, Davydov et al. (2010) were also able to consider how these shorter, ~100ky cycles are packaged into ~400 ky cycles. This packaging is consistent with the interpretation of Raymond C. Moore, cited in (Wanless and Shepard, 1936). We recalculated boundary ages for both the SW US and the Donets Basin using a Bayesian model (Keller, 2018) (Fig. 2; Fig. 3). This model produces an age-depth estimate by considering uncertainties on dates and stratigraphic position of dated layers and refines these uncertainties by assuming that dates cannot violate the principals of stratigraphic superposition. Model outputs and uncertainties of undated horizons provide an error envelope that can be used to estimate cycle duration and the ages of biostratigraphic boundaries. The results are similar to those presented in the original studies (Davydov et al., 2010; Rasbury et al., 1998). Rather than a linear model this tests the assumption of equal duration cycles, which would require the slope of each segment is the same within uncertainty. For the case of U—Pb dating of zircons, the errors are small and with the numerous cycles and ages there is little doubt that the cycles represent

Period	Cycles	U-Pb Ages
Pennsylvanian	33	307.26±0.11 Ma
		310.55±0.1 Ma
		312.01±0.08 Ma
		312.23±0.09 Ma
		313.16±0.06 Ma
Mississippian	137	314.4±0.06 Ma
Mississippian	138	328.14±0.1 Ma
Mississippian	30	342.01±0.1 Ma
		345.0±0.08 Ma
		345.17±0.07 Ma
Mississippian	120	357.26±0.08 Ma



**Fig. 2.** Simplified stratigraphic column from a cyclothem record in the Donets Basin, Ukraine using cycles as a counting metric, rather than thickness. U—Pb ages measured in zircons from interstratified tuffs; errors reported in  $2\sigma$  (Davydov et al., 2010). Graph (right) shows U—Pb zircon derived stratigraphic Bayesian age-cycle model for the Donets Basin. Model uses stratigraphic position as a priori to refine uncertainties in dates (Keller, 2018). Uncertainty envelope represents 95% confidence interval of the age model. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Period	Cycles	U-Pb Ages
Permian	16	298±1.4 Ma
Carboniferous	16	300±3.8 Ma
	2	298±18 Ma
		291±15 Ma
	13	286±14 Ma
		303±10 Ma
	4	306±3 Ma



**Fig. 3.** Simplified stratigraphic column from cyclothem section in the Sacramento Mountains, NM with ages from the Central Basin Platform of the Permian Basin, Texas. U—Pb ages measured in paleosol calcite (Rasbury et al., 1998) and marine cement (Rasbury et al., 2004); errors reported are  $2\sigma$ . The stratigraphic Bayesian age-depth model uses stratigraphic position as a priori to refine uncertainties in U—Pb paleosol dates (Keller, 2018). Uncertainty envelope represents 95% confidence interval of age model. The dashed line and bracketing red lines are an age-cycle model derived from linear regression (York and Evensen, 2004) (referred to as York fit) through the U—Pb paleosol data, similar to what Rasbury et al. (1998) used to estimate cycle durations and boundaries. The York fit assumes equal cycle durations. Cycle durations and ages are similar between the models. Errors for the Bayesian model are larger because it does not assume a linear fit or equal cycle duration. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

equal time (Fig. 2). In the case of the U—Pb dating of carbonates, the errors are mixed, with some better than 1% errors and others approaching 10% errors. In this case the Bayesian model has inflated errors over a linear fit (York and Evensen, 2004), and may better reflect the real uncertainties since there is no underlying assumption of equal cycle durations. The linear model used by Rasbury et al. (1998) yielded a more precise age for the Carboniferous-Permian boundary ( $301 \pm 2$  ( $2\sigma$ )) than the Bayesian model does ( $300.7 \pm 3.95$  ( $2\sigma$ )), but the boundary ages are the same within uncertainties (Fig. 3).

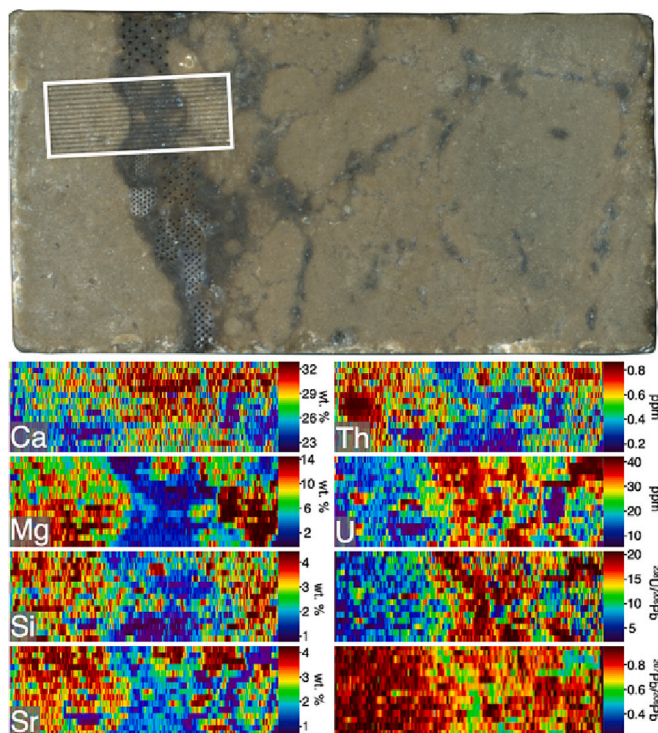
### 3.3. Comparison between isotope dilution and LA U—Pb ages of calcretes

Laser ablation mapping of sample X-1-1 from a core from the Central Basin Platform of the Permian Basin studied by Rasbury et al. (1997) confirms the clear relationship of U with dark brown, organic rich (smells like crude oil when broken) rhyzolite calcite (Fig. 4). The host rock is lighter brown dolomite, which is easily seen in the Mg map. Si, Sr and Th all have higher concentrations in the dolomite than the calcite (Fig. 4). The  $^{238}\text{U}/^{206}\text{Pb}$  is higher in the calcite and the  $^{207}\text{Pb}/^{206}\text{Pb}$  is lower in the calcite, consistent with elevated U and ingrowth of  $^{206}\text{Pb}$  (Fig. 4).

Laser ablation maps using the Drost approach in Iolite4 (Paton et al., 2011) for extracting and pooling pixels provides a framework for interpreting LACarb ages. The pixels correspond to duty cycles. The rate that the sample is moving under the laser is  $20 \mu\text{m/s}$  and with the

counting time it represents close to a second. The spot size is  $80 \mu\text{m}$  so the pixels are about  $20 \times 80$  microns in plan view and nearly  $10 \mu\text{m}$  deep. To select for calcite, we chose a criterion of elevated counts of Ca and low counts for Si. This produced 2122 pixels. The pixels were subdivided into 50 pools based on probability on  $^{238}\text{U}/^{208}\text{Pb}$ . We chose this ratio for pooling because it allows us to achieve the greatest spread in U/Pb without the bias that might be introduced by using the  $^{238}\text{U}/^{206}\text{Pb}$ . We left out 10% from the lowest and highest ends (as recommended by Drost et al., 2018) and plotted the remaining 40 data points on a Tera-Wasserburg plot using IsoplotR model 3 (Vermeesch, 2018) (Fig. 5). This yields an age of  $295 \pm 9$  Ma ( $2\sigma$ ), which is entirely consistent with the published ID TIMS age of  $298.4 \pm 1.4$  Ma ( $2\sigma$ ) (Rasbury et al., 1998), albeit the uncertainty is 10 times higher. To be sure, instruments with higher sensitivity could easily half the uncertainty we obtained by LA ICPMS, and it is encouraging that the result is accurate. It is worth discussing how we reduced this data since there are many different approaches that are being taken. In fact, our approach is evolving as we try new things. We used the NIST612 glass as the primary standard. We tuned with NIST612 to maximize signal and minimize oxides and doubly charged ions. We did a final tune with WC-1 using the gas flow and torch position to tune for the  $^{238}\text{U}/^{206}\text{Pb}$  ratio, which should be about 23 based on isotope dilution (unpublished and Roberts et al., 2017). For each session, we run WC-1 (Roberts et al., 2017) and Barstow (Rasbury et al., 2021) as secondary standards and we look at the results in Iolite4 to make sure that the ratios on WC-1 are reasonable and that the spread





**Fig. 4.** Slab of sample X-1-1 with a white box showing the LA mapped area. The image is  $\sim 1$  cm across. Element maps below are output from Iolite4 and were used to select pixels for isochron plots. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in Barstow gives the correct age within uncertainty. For the data presented here, we did not need to make a correction for these secondary standards. That is, the ratios used are the ratios produced using NIST612 as the primary standard and putting the data through the U–Pb Geochronology DRS in Iolite4. This subtracts the baseline, corrects for downhole fractionation (which is negligible with line scans) and then makes a final correction for fractionation and drift in the signal.

In addition to the calcite, we extracted pixels from the host dolomite. Based on petrography, the dolomite is older than the calcite, which crosscuts the dolomite (Rasbury et al., 1997). Pixels were selected using elevated Mg concentrations. This produced 3900 pixels that were subdivided into 99 bins (the maximum allowed on Iolite4) based on probability on  $^{238}\text{U}/^{208}\text{Pb}$ . Trimming the low and high 10%, we are left with 78 (throwing out one additional spot with an anomalous U/Pb error) that give an age of  $351 \pm 13$  Ma ( $2\sigma$ ) on a Tera-Wasserburg plot (Fig. 5). The sample is from the lower Permian and cannot be older than 300 Ma, and thus this age is far too old even outside the uncertainty. The  $^{238}\text{U}/^{208}\text{Pb}$  versus U concentration shows that there are two populations of dolomite. The segment with the lowest U concentrations shows a spread in the  $^{238}\text{U}/^{208}\text{Pb}$  without change in the U. This demonstrates that common Pb is more important in this segment than in the other segment, which shows a strong positive correlation between the  $^{238}\text{U}/^{208}\text{Pb}$  and U concentration (Fig. 5A). The boundary between these two populations is at a  $^{238}\text{U}/^{208}\text{Pb}$  of about 3 (Fig. 5A). Taking only the data points above  $^{238}\text{U}/^{208}\text{Pb}$  of 3 ( $n = 42$ ), the age on the Tera-Wasserburg plot is  $318 \pm 23$  Ma. While the nominal age is still slightly old, it is accurate within uncertainty. Without the temporal constraints provided by biostratigraphy and calcite dates, which place the maximum age of this sample at 300 Ma, it would be permissible to interpret the date calculated using all the data as the true sample age. Alternatively, given the prior knowledge of the maximum sample age we could anchor these data to produce an age of 300 Ma. However, this technique prevents the dolomite date from providing a truly

independent age constraint, highlighting the importance of being forthcoming when using anchors and providing context for why the anchor was chosen. In many scenarios, filtering data by other isotopic or elemental ratios could reveal distinct populations that would allow geologists to better assess reasons for inconsistent ages or scatter in data.

### 3.4. Assessing the potential for U–Pb carbonate ages to predict cyclothem duration

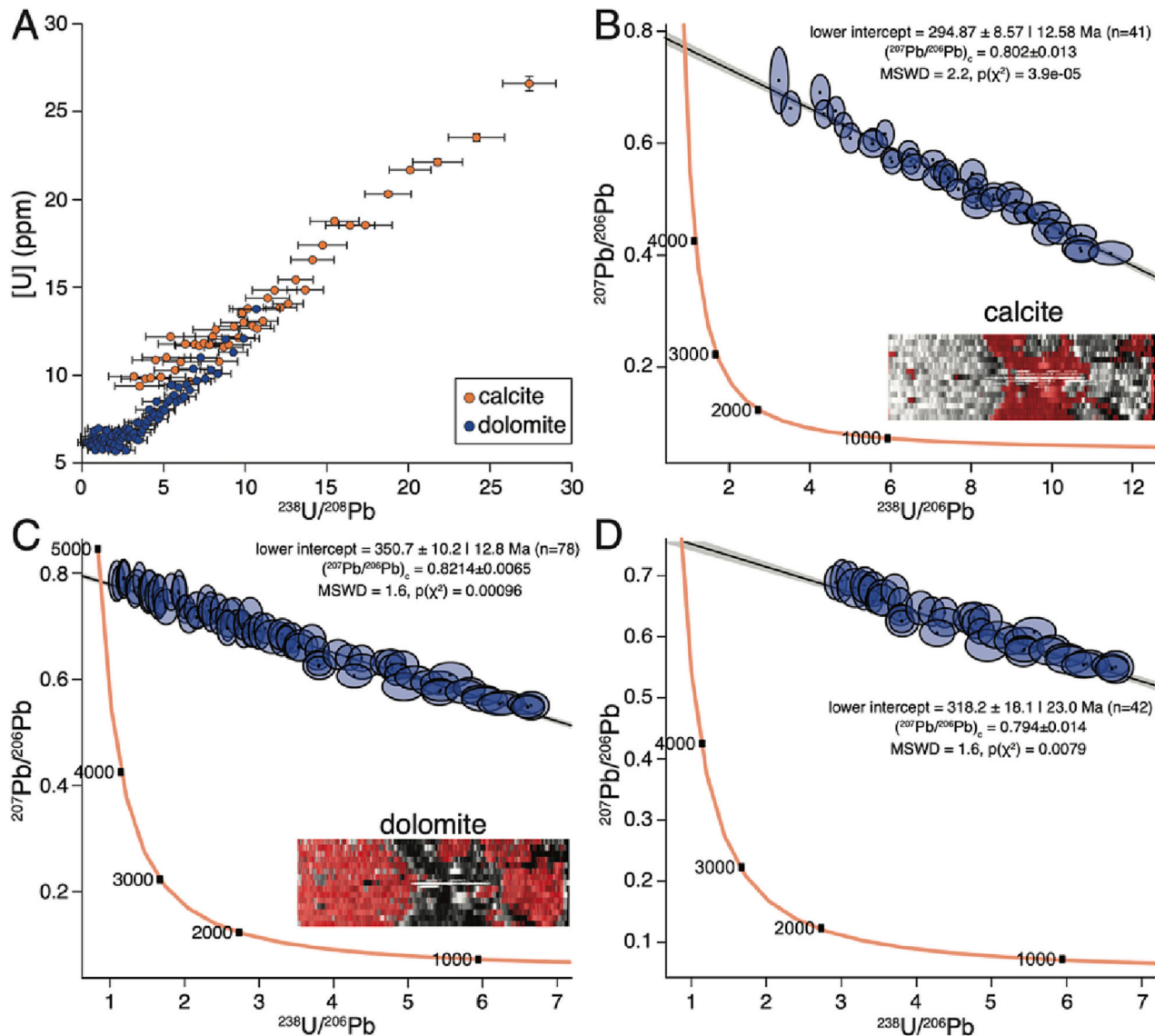
Even the highest age precision will not be able to date all scales of cyclicity, so techniques to extrapolate ages and estimate duration of cycles are needed. Certainly, lower calculated uncertainties (precision) suggest a more reliable (accurate) estimation of the real age of a deposit. However, reconstructing the timing of deposition within a stratigraphic sequence is also complicated by the uncertainty imparted by interpolating between age tie-points. Therefore, the precision of deposition age estimates is dependent not only on the precision of individual dates, but also on the number and distribution of ages within the stratigraphic sequence. Age-depth models derived from traditional dating techniques (i.e. zircon U–Pb and sanidine Ar–Ar) benefit from high-precision on individual dates, but are often dependent on the distribution of tephra within the sedimentary sequence, and can suffer from poor stratigraphic coverage. Conversely, dates of carbonate horizons are generally far less precise than zircon or sanidine dates, but carbonates are ubiquitous in the sedimentary record, and, therefore, may offer the opportunity to fill in gaps in chronology, especially as techniques in LACarb evolve towards higher precision and throughput.

To explore how LACarb ages can benefit temporal characterization of cyclothem, we simulate the precision and accuracy of deposition age estimates given variable numbers of LACarb dates. This model simulation randomly selects the stratigraphic positions of  $N$  samples within a stratigraphic section containing 200 cyclothem of assumed equal duration. In this particular simulation we input cyclothem of 100 kyr duration. Uncertainties in the stratigraphic position of the carbonates are set within a range of  $\pm 10$  cycles ( $2\sigma$ ): a number based on the estimated ability for geologists to place a sample in vertical space within a section with 95% confidence. Uncertainties in carbonate ages are set to a range of  $\pm 9$  Myr ( $2\sigma$ ), equivalent to 3% standard error for 300 Ma for LACarb analyses. The simulation assumes a normal distribution for the cycle positions and the respective carbonate ages. We then use a linear regression (York fit) that accounts for errors in both  $x$  and  $y$  variables (York and Evensen, 2004) to simulate our ability to recover the true cycle duration (the slope of the best-fit line) and age distribution along the line. A Monte Carlo simulation repeats this experiment of  $N$  LACarb ages, randomly placed within this section, 5000 times. This allows us to calculate (1) the expected standard error for the age of a horizon within the section and (2) the expected standard error for the cycle duration, given  $N$  LACarb ages randomly placed within the section. The precision of both cycle duration and horizon age estimate increases with increasing number of U–Pb age tie-points within a sequence (Fig. 6). As the number of LACarb ages increases to above 10 samples, the precision of depositional age estimates for individual stratigraphic horizons approaches 1% ( $2\sigma$ ) error (Fig. 6A). Similarly,  $\sim 10$  LACarb ages allows for estimates of cycle duration of  $\pm 30$  kyr ( $2\sigma$  uncertainty), which is better than half a cycle for the 100 kyr cyclothem (Fig. 6B).

As LACarb methods and standards continue to improve, greater levels of precision may be possible in the future. To illustrate this scenario, we repeated the simulations by assuming that LACarb analyses could reach 1%  $2\sigma$  error (dashed curves in Fig. 6a,b). In this case, 15 LACarb ages in a stratigraphic section containing 200 cyclothem would allow for cycle duration estimates to  $\pm 9$  kyr ( $2\sigma$ ).

Using the same approach, but with uncertainties of 0.1 Ma ( $2\sigma$ ) for U–Pb zircons, it takes far fewer ages to achieve much better precision for cycle durations (Fig. 6C; 6D). This experiment provides an example for a single stratigraphic section with the underlying assumption of equal cycle durations. In typical stratigraphic sequences, stratigraphic



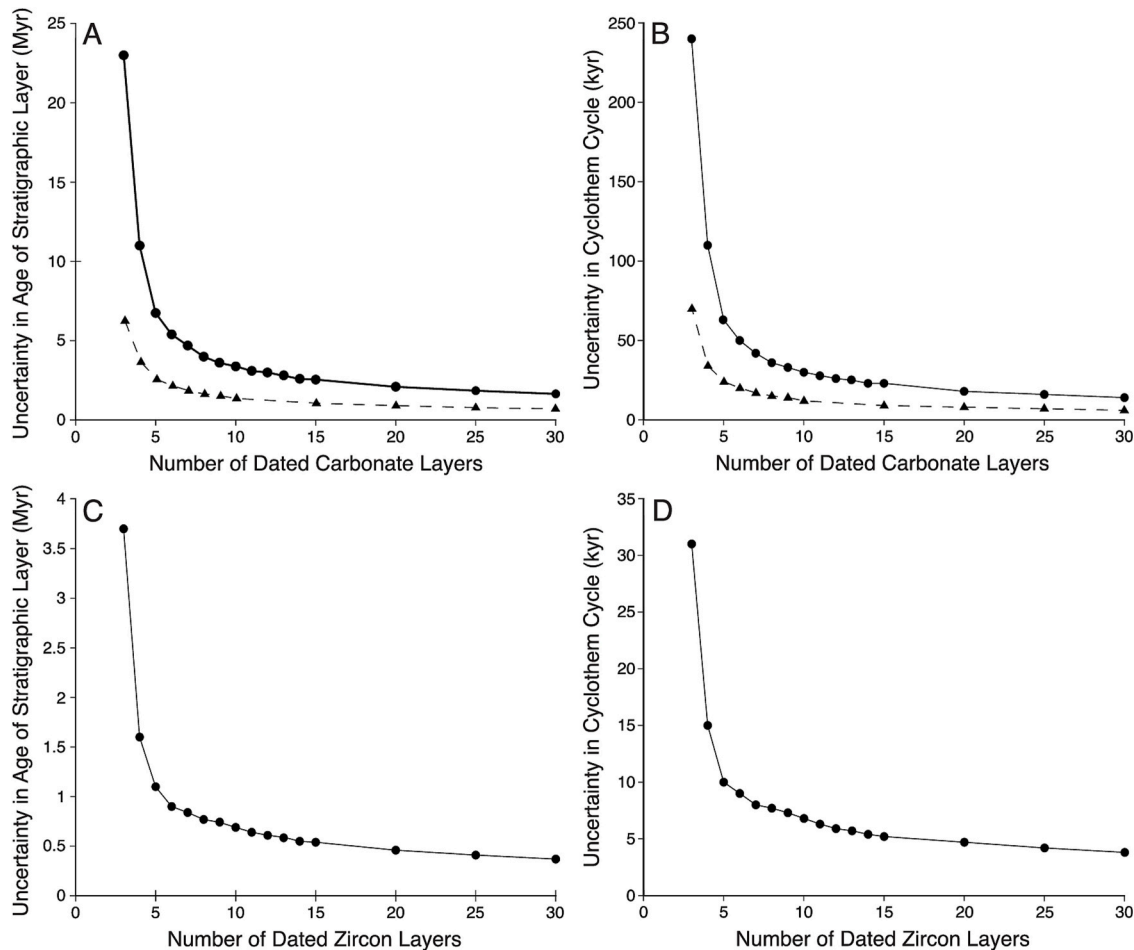


**Fig. 5.** U–Pb Analyses of calcite and dolomite in sample X-1-1. A.  $^{238}\text{U}/^{208}\text{Pb}$  versus U concentration shows a clear difference between calcite, which was selected based on high Ca and low Si, and dolomite, which was selected based on high Mg concentrations. The dolomite shows two domains: the low end is a near horizontal line showing that the range in  $^{238}\text{U}/^{208}\text{Pb}$  results from a range of Pb concentrations, while the domain that has higher  $^{238}\text{U}/^{208}\text{Pb}$  shows a strong positive relationship between  $^{238}\text{U}/^{208}\text{Pb}$  and U concentrations showing that, for this domain, the range is due to the range in U concentrations. B. The Tera-Wasserburg plot was output from IsoplotR using model 3, and shows data subdivided from the red calcite pixels and pooled based on the  $^{238}\text{U}/^{208}\text{Pb}$ . C. The inset is a map of the sample with dolomite shown by red pixels. The Tera-Wasserburg plot (as above) shows all the data from the subdivided dolomite pixels. The age derived from these data of  $350.7 \pm 10.2$  is too old. D. Tera-Wasserburg plot derived using only the data above  $^{238}\text{U}/^{208}\text{Pb}$  of 3 based on the change of slope in (A). These data give the correct age within uncertainty. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

position is defined by depth of dated layers above the surface, and uncertainty is based on layer thickness estimates. However, when constructing models describing cyclothem ages, we recommend to instead describe the stratigraphic position of dated layers by their cycle position in the section. That is, set the base of the stratigraphic column as cycle 0 and assign a cycle number to each cycle top. Cycle counts are based on careful analysis involving the recognition of cyclothem patterns. We demonstrate this approach both in our reanalysis of cyclothem in the Urals and Sacramento Mountains (Fig. 2; Fig. 3), as well as in our idealized cyclothem simulations (Fig. 6). Defining stratigraphic position based on cycles rather than thickness is a reasonable approach because while the packages can have vastly different thicknesses, the cycles are easy to identify, and it is reasonable to assume they are paced by some periodic function such as Milankovitch cycles. However, this approach assumes the number of cycles is known. Boundaries not identified can

mean there are amalgamated cycles. Additionally, cycles with different durations can present similar facies patterns such that extra cycles may be identified. The better constrained the 3-dimensional depositional stratigraphy is known the greater the confidence in cycle counting. Using cycle number (cycle superposition) frees one from applying this to a single section or keeping the measurements to the same depositional position and facies.

The synthetic experiment in Fig. 6 provides the expected precision of recovering 100 kyr cycles in a 200-cycle section. But what if the section contained 200 cycles that involved other Milankovitch cycle durations, such as 18 kyr, 41 kyr, or 400 kyr? Would it be possible to still resolve these cycle durations? To test this, we performed a set of simulations using 200 cycles of constant duration of 18 kyr, 41 kyr, 100 kyr, and 400 kyr, respectively (Table 2). For these simulations we tested just 10 LACarb ages with 3%  $2\sigma$  standard error. We also tested 10 LACarb ages



**Fig. 6.** Simulation of precision of LACarb and tephra derived cyclothem age estimates. A. Monte Carlo simulation of uncertainty in age estimates reported as  $2\sigma$  absolute standard error on a 310 Myr stratigraphic horizon based on an increasing number of dated carbonate layers in an idealized section containing 200 cycles of 100 kyr duration. Solid line with circular markers shows stratigraphic layer uncertainties derived from LACarb ages with  $2\sigma$  standard error values of 9 Ma; dashed line with triangle markers shows stratigraphic layer uncertainties derived from LACarb ages with  $2\sigma$  standard error values of 3 Ma. B. Monte Carlo simulation of uncertainty in cycle duration reported as  $2\sigma$  absolute standard error on a 100 kyr cyclothem cycle duration based on a variable number of dated carbonate layers in an idealized section. Solid line with circular markers shows cycle duration uncertainties derived from LACarb ages with  $2\sigma$  standard error values of 9 Ma; dashed line with triangle markers shows cycle duration uncertainties derived from LACarb ages with  $2\sigma$  standard error values of 3 Ma. C. Monte Carlo simulation of uncertainty in age estimates reported as  $2\sigma$  absolute standard error on a 310 Myr stratigraphic horizon based on an increasing number of dated tephra deposits with high-precision zircon ages in the same idealized section as for carbonates. D. Monte Carlo simulation of uncertainty in cycle duration reported as  $2\sigma$  absolute standard error on a 100 kyr cyclothem cycle duration based on a variable number of dated tephra layers in an idealized section. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 2**  
Simulated achievable age precision of cyclothem cycles paced by different Milankovitch cycles using LACarb. Values assume 10 LACarb ages in a cyclothem made up of 200 cycles.

Cycle Duration (kyr)	$2\sigma$ Individual Layer Uncertainty (myr)	$2\sigma$ Cycle Uncertainty (kyr)
<b>10 LACarb ages with <math>\pm 9</math> Ma (<math>2\sigma</math>) uncertainties in a 200-cycle sequence</b>		
18 kyr	3.34	30
41 kyr	3.3	30
100 kyr	3.4	30
400 kyr	4.7	42
<b>10 LACarb ages with <math>\pm 3</math> Ma (<math>2\sigma</math>) uncertainties in a 200-cycle sequence</b>		
18 kyr	1.1	10
41 kyr	1.16	10
100 kyr	1.38	12
400 kyr	3.38	29

with the higher precision of 1%  $2\sigma$  standard error. We find that the standard deviation in cycle duration is essentially the same for all cases, with the 400 kyr cycles yielding slightly larger absolute uncertainties

(Table 2). This near invariance of uncertainties in cycle duration is also the case for the uncertainty in horizon ages. The implication from these findings is that 400 kyr and 100 kyr cycles can be identified. However, 18 kyr and 41 kyr cycles cannot be discriminated from one another. On the other hand, higher precision LACarb ages with 1%  $2\sigma$  standard error yield cycle duration uncertainties of  $\pm 10$  kyr ( $2\sigma$  standard error) for the 18 kyr and 41 kyr cycles. Thus, such higher precision LACarb ages will make it possible to resolve the difference between 18 kyr and 41 kyr (Table 2) and allow for the identification of higher frequency cyclothem.

Application of a linear regression and use of cycle number assumes that the cycle duration is the same, on average, throughout the section. This assumption works for making the point in Fig. 6, but we recommend using a Bayesian model on real data. The Bayesian model eliminates the need to assume the cycles are of equal duration and actually tests that assumption. However, the linear modeling provides a powerful predictive tool in planning one's approach to field sampling, and for understanding the limitations of data sets of a certain size. Will five more samples make a large difference in uncertainties or a negligible change?

This approach takes advantage of what we do know about stratigraphic sequences and can be used as a predictive tool to determine the minimum number of cycle age dates needed for lowest age uncertainties. The solution depends on the number of cycles within the given duration of section of interest.

### 3.5. Using stratigraphic constraints to refine depositional age models

Layering and cycles in carbonates range from years to millions of years. There will always be a limit on what cycle durations can be directly constrained. For using LACarb to date 100ky cycles, which many have attributed to the cyclothem, age modeling is required for determining average duration of cycles over a long interval, with age-depth models or age-cycle models. Age-depth models are fraught with uncertainties due to varying layer thicknesses. The thickness of a depositional cycle of any scale will vary greatly through the 3-dimensions of a cyclic package. Maintaining the same depositional and facies position from cycle to cycle commonly cannot be done in a single vertical section and requires a well constrained 3-D cycle stratigraphy. To avoid the issue due to depth/thickness variations we recommend applying cycle-age models instead of or in addition to age-depth models. The predictive model in Fig. 6 required the assumption that all cycles are the same duration (whatever that is), and that all the cycles are included. The linear regression method that we use (York and Evensen, 2004) does account, however, for uncertainties in cycle position ( $2\sigma$  standard error of  $\pm 10$  cycles). Nevertheless, techniques that do not require such assumptions of constant cycle duration, like the Bayesian model of Keller (2018), are needed.

Refining the uncertainties of stratigraphic age models using the principal of superposition can increase the level of precision on carbonate generated age-stratigraphic models because it utilizes the greater stratigraphic coverage achievable through LACarb to decrease the uncertainty on individual age tie-points (Montano et al., 2022). The idea behind using the constraint of superposition to refine stratigraphic models is that individual dated layers or cycles cannot be older than layers or cycles below them, nor younger than layers above them. Therefore, models can be trained to reject ages that violate the superposition constraint, based on the dates of layers above and below them. Examples of other studies that have utilized this approach for stratigraphic age models include Guex et al. (2012), Haslett and Parnell (2008), and Meyers et al. (2012). The Chron.il software uses Bayesian Markov chain Monte Carlo model to refine age-depth estimates with the superposition constraint (Keller, 2018). The main input parameters for Chron.il are stratigraphic age-tie points, stratigraphic height, and their respective uncertainties. An example of the use of this model, with a detailed description of the approach can be found in the supplement of (Schoene et al., 2019). Further, while not explored in this review, Chron.il can also incorporate estimates for hiatuses in deposition (as detailed in Deino et al. (2019)), which can be useful for defining stratigraphic age models where unconformities are identified by field relationships.

We used Chron.il to generate cycle-age models by describing stratigraphic position in terms of cycle numbers. The Chron.il model does not assume a constant deposition (or cycle period) rate, but instead allows one to consider details of cycle stacking. That is, changes in slope when this model is used with cycles instead of stratigraphic thickness shows either missing cycles, or perhaps that cycles do not represent the same duration. If one had continuous data, a missing cycle would show up as an offset of the line. With fewer data points, this would show up as a change in slope. For example, in Fig. 2B there is an offset in the curve that occurs where Davydov et al. (2010) recognized missing section in the Donets Basin relative to the Urals based on biostratigraphy.

To further explore the application of statistical fits to age-cycle models of cyclothem, we apply Chron.il to two modeled stratigraphic columns. One section has 5 randomly generated age tie-points and the other has these same 5 points plus an additional 5; age uncertainties are within the range currently expected with LACarb (we anticipate these

uncertainties will improve) for both simulations (Fig. 7). We also apply the linear regression (York and Evensen, 2004) to both sets of data. This experiment is meant to simulate a reasonable estimate of the precision and accuracy of cyclothem age-depth modeling generated by LACarb dated stratigraphic layers and to show the model improvement that comes with a greater number of LACarb dated horizons that are randomly located within the section. With only 5 samples, the application of Chron.il provides a higher confidence in model ages than the linear regression (Fig. 7A). However, with 10 LACarb ages, the linear regression predicts a higher confidence level (Fig. 7B). This higher confidence level is likely an artifact of the embedded assumption of constant cycle duration (constant slope) for the linear regression method.

The ability to place a local, 2-dimensional stratigraphic column in a 3-dimensional context, provides a higher confidence level in cycle packaging, including where cycles are amalgamated or eroded. The 3-dimensional framework also offers a natural test of dating the same cycles in different locations. Sequence stratigraphic packages come in many sizes. Most of the underlying processes that could drive these scales of cycles are dependent on the duration of the cycles. Therefore improved age constraints of cycles will advance testing of driving forces. While 3–5% uncertainties on a given boundary provide only a coarse constraint, multiple ages within a section can test the average duration of packages (cycles) and refine our understanding of processes that built them. It is notable that dated records of cyclothem appear to point to an approximately 100ky cycle, similar to what is seen in the Pleistocene. Prior to age dating a consensus was growing that cyclothem were 400ky cycles (Heckel, 2008). While the uncertainty on the average estimates based on carbonates are large, they clearly distinguish cyclothem from 400ky cycles. It is clear that LACarb has great potential for refinement of strata ages and for testing the orders of packages within those strata.

## 4. Suggested best practices for obtaining LACarb dates of sequence stratigraphic units

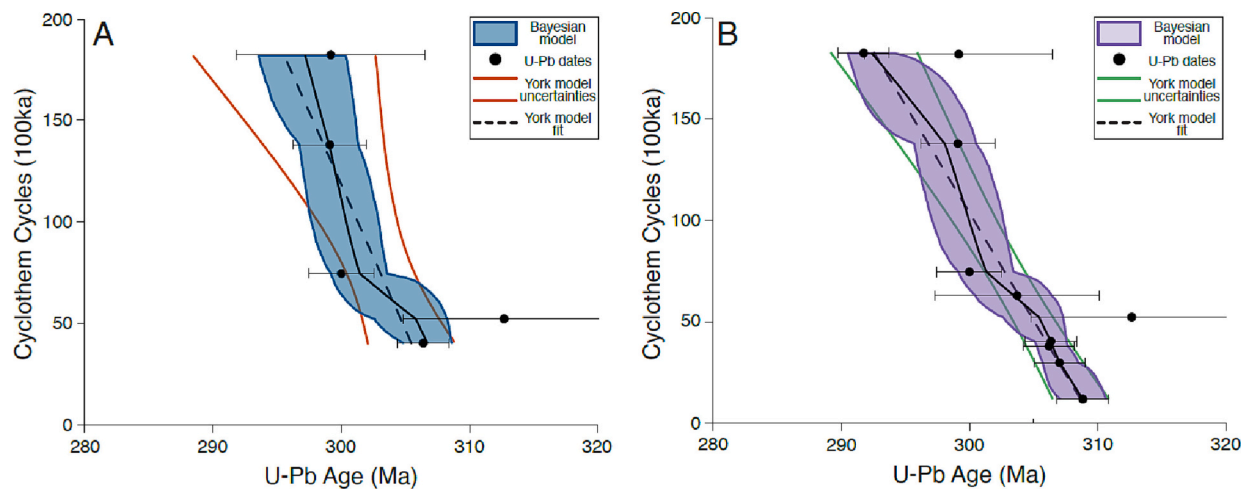
The application of LACarb dating to place time constraints on the sedimentary rock record is a burgeoning geochronologic technique. While previous review papers have covered LACarb methods (e.g. Roberts et al., 2020), we add here notes and suggested best practices for applying LACarb dating to sequence stratigraphy.

### I. Field work and sample collection:

- Stratigraphic sequences are 3-dimensional bodies that are often incomplete in individual vertical outcrops. Two-dimensional cross sections (i.e., Eros et al., 2012; Montañez, 2022) are better to capture details. However, the gold standard of sample collection, is to collect multiple samples from a single bed or unit in the 3-dimensions of a stratigraphic sequence.
- To expand on point a: It is important to note that each individual stratigraphic section, on average, will have more gaps in deposition than units (Wilson, 1975).
- Due to the ability to statistically refine age-depth models, it will often be more important to measure more samples distributed through the section than having fewer high-resolution dates.

### II. For sample characterization prior to measuring U—Pb ages:

- Carbonates can readily be altered after initial deposition. Therefore, carbonate U—Pb dating requires constraints on diagenesis of components being dated, cross-cutting relationships and superposition at all scales (i.e. sequences to diagenetic cements).
- It is not necessary to strictly measure unaltered carbonates. For example, most marine cements in the Phanerozoic require pre-existing cavities, and paleosols require that sediments have been exposed through erosion. Rather, carbonate U—Pb



**Fig. 7.** Idealized LACarb generated age-depth model using Chron.jl and York fit. A. Five randomly generated LACarb dated stratigraphic horizons. Solid black line indicated stratigraphic age model generated with Chron.jl, with  $2\sigma$  error window indicated by blue envelope. Dashed black line indicates York fit cycle-age model, with  $2\sigma$  error window shown in red. Age uncertainties reported as  $2\sigma$  absolute standard error. D. Ten randomly generated LACarb dated stratigraphic horizons. Ages include the 5 dates from A, plus five new dates. Stratigraphic age model derived from Chron.jl and York fit, as in (A). Uncertainties reported as  $2\sigma$  absolute standard error. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

dating requires careful determination of the individual events recorded in a sample so that age-estimates can be placed in a proper geologic context (e.g. [Brigaud et al., 2021](#); [Montano et al., 2022](#)).

### III. For measuring U—Pb ages and stratigraphic age-depth models:

- It can often save time and resources to determine which, if any, components of a sample have U/Pb ratios suitable for U—Pb dating, prior to making measurements. The easiest method to pre-screen samples is to generate LA maps of high U, low Pb areas.
- Measuring U and Pb from an individual fabric within a sample can be done using a LA map in the Iolite4 software, which allows the analyst to select individual pixels within the image based on user defined criteria (e.g. elemental concentrations, or ratios) (method described in [Drost et al., 2018](#)).
- Individual LACarb dates do not need to have the highest possible precision to be useful in defining a stratigraphic age model. The greatest strength offered by carbonate U—Pb dating for adding temporal constraints in sequence stratigraphy is likely to be the ability to generate large numbers of dates for a given section.
- The precision of carbonate derived age-depth models is likely to benefit from the additional constraint of stratigraphic superposition to refine uncertainties on individual dates. Chron.jl ([Keller, 2018](#)) is a publicly available software that outputs a Bayesian age-depth model incorporating stratigraphic position of dated layers.

## 5. Conclusions and perspectives

The sedimentary rock record is the primary archive of the evolution of climate and life. The climate record comes from plant and animal fossils and carbon compounds that are preserved in the record that can be used as proxies for environmental conditions. The chemostratigraphic record preserved in marine carbonates not only provides a framework for correlation, but also contains details of the processes and responses to changes. Fossils found within sedimentary sequences are the record of first and last appearances, extinction events, and evolution of animals and plants. These rich archives are deposited in stratigraphic sections, which often do not have recognizable volcanic ash deposits, and can, therefore, be better characterized through the addition of carbonate U—Pb dates.

The stacking pattern of sedimentary strata can also help to unravel details of sea level change and tectonics: processes that respond to and/or drive environmental change. In terrestrial environments changes in lake level or fluvial processes are also tied to climate and tectonics. Testing hypotheses of processes that produce stacking patterns requires age constraints. Correlations between records, particularly marine and terrestrial records is key to understanding these underlying influences. While volcanic ashes are increasingly recognized in the sedimentary record and type sections have increasingly well-defined ages, there remain many uncertainties in correlations which techniques such as U—Pb dating of *syn*-sedimentary carbonates can help to address.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.earscirev.2023.104495>.



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