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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 basinal 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-eustacy, 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 flower precision dates throughout a stratigraphic section provide age constraints that can be similar in precision to a few high precise ages, depending on the stratigraphic distribution throughout the section.

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1. Introduction

The questfions we are askfing of the rock record create a great demand for fimproved tfime resoflutfion. Thfis demand fis hfighflfighted by the Natfionafl Academfies 'A Vfisfion for NSF Earth Scfiences 2020-2030: Earth fin Tfime' (2020), whfich descrfibes a need for better temporafl constrafints to test geoflogfic modefls. Thfis fis especfiaflfly true fin the carbonate rock record, and for sequence stratfigraphfic archfitectures. Sequence stratfigraphy and cycfle stratfigraphy fin carbonate formatfions fincreasfingfly reveafl finformatfion about temporafl and spatfiafl changes fin deposfitfionafl envfironments, and push our understandfing of potentfiafl drfivers, such as eustatfic sea flevefl. However, there fis sfiffl a scarcfity of geochronoflogficafl constrafints to test cycfle duratfions and provfide constrafints on rates of sedfimentatfion. Through contfinufing advances fin anaflytficafl techfniques and approaches to sampflfing, the current state of U−Pb datfing of carbonates makes the goafl of wfidespread absoflute datfing of carbonate stratfigraphy more possfibfle than ever before. These advances occur on the back of decades of U−Pb deveflopments and wefll over a century of deveflopfing concepts of carbonate sequence stratfigraphy (before fit was caflfled that). We brfieffly revfiew thfis hfistory to provfide context for current advances and suggest dfirectfions for future appflficatfions of carbonate geochronoflogy to sequence stratfigraphy.

A sfignfficant portfion of shaflflow carbonate rocks, fif not afll, preserve rhythms of deposfitfion recorded by 3-dfimensfionafl facfies dfistrfibutfions. Superposfitfion, cross cuttfing reflatfionshfips and stratfigraphfic changes fin vertficafl thficknesses and flaterafl facfies dfistrfibutfions deffine cycfles of many scafles commonfly wfith mufltfipfle hfierarchfies. Such detafifls fin Late Pafleozofic cycflothems have been recognfized and studfied for over a century (e.g., Ffiefldfing, 2021; Montañez, 2022; Wanfless and Shepard, 1936). Durfing the 1950s through 1970s wfith fimproved understandfing of carbonate facfies, cycfles and sequences were fincreasfingfly recognfized fin most pflatform carbonates, as exempflfiffied fin the syntheses of Wfiflson (1975). At thfis tfime, fit was reaflfized that the facfies dfistrfibutfion and extent of carbonates are sensfitfive to sea flevefl and foflflow the "prfincfipfle of fast but rapfid deposfitfion" such that carbonate strata are flfikefly domfinated by perfiods of non-deposfitfion (Wfiflson, 1975).

The advent of sefismfic sequence stratfigraphy fuefled the use of onflap and offflap of strata to provfide a record of regfionafl sea flevefl change (Vafifl et afl., 1977). By comparfing basfins across the gflobe fit appears possfibfle to puflfl out the eustatfic sfignafl (e.g. Haq and Schutter, 2008). Usfing fusuflfinfid bfiostratfigraphy and onflap-offflap sequences, Ross and Ross (1985) argued that Late Pafleozofic 1–5 Ma sequences responded to eustatfic changes fin sea flevefl and were 'synchronous and worfld-wfide'.

After reffinements by Van Wagoner et afl. (1988), use of sequences and termfinoflogy to descrfibe thefir components became more wfidespread. Sequence stratfigraphfic anaflysfis on carbonate rocks reached a renewed flevefl that contfinues to the present. Durfing thfis tfime, two of many fimportant pofints wfith respect to thfis paper became more recognfized. 1) The dfifferent scafles of stratfigraphfic packagfing or archfitecture were deffined by 3-dfimensfionafl cycfles and that sfingfle vertficafl sectfions aflone are finsuffficfient to deffine the cyclflicfity (e.g. Kerans and Tfinker, 1997). 2) The packagfing of the cycfles dfiffers durfing ficehouse and greenhouse tfimes (Read et afl., 1995; and see Montañez, 2022; Ffig. 4 for current vfiew).

By 2000, our flevefl of understandfing of hfierarchficafl cycfles fin carbonates was becomfing qufite sophfistficated. Thfis understandfing was dependent on sea-flevefl curves and proxfies whfich have become fincreasfingfly better understood. Correflatfions, bfiostratfigraphy, chemostratfigraphy and sea flevefl trends were and are determfined from carbonate strata and carbonate mfinerafls. However, most sequences were undated so that scafles of cycfles and gflobafl correflatfions were untested by geochronoflogy. The Carbonfiferous-Permfian boundary as an excefllflent exampfle that fis pertfinent to thfis paper. Harfland et afl. (1990) Geoflogficafl Tfimescafle reported the Carbonfiferous-Permfian boundary at 290 ± 20 Ma (2σ), an uncertafinty that precfludes answerfing many questfions we ask of the stratfigraphfic record, flet aflone of any meanfingfufl tfime anaflyses.

Prfior to the mfid 1980's radfiometrfic age dates for carbonate strata oflder than Pflefistocene were on mfinerafls fin ashes, voflcanfic flayers, and fintrusfions. The earflfiest work on datfing carbonates used Pb−Pb to date Archean stromatoflfites (Moorbath et afl., 1987). Whfifle the Pb−Pb was flater shown to flfikefly resuflt from Pb mfineraflfizatfion and was thus not a prfimary age (Sumner and Bowrfing, 1996), thfis spurred the ffirst U−Pb carbonate race, as a number of papers usfing U−Pb foflflowed and showed the great potentfiafl for provfidfing fimproved tfime constrafints (summarfized fin Rasbury and Cofle, 2009). Thfis earflfier work used fisotope dfiflutfion (ID) whfich fis tfime consumfing and flacks opportunfitfies for prescreenfing for favorabfle sampfles, whfich sflowed advances. Determfinfing whfich sampfles mfight work was fimproved somewhat wfith fimagfing techfniques flfike phosphor fimagfing (Cofle et afl., 2003), but hfigh uranfium fis not the onfly key to success and thfis fimagfing dfid not address the Pb content.

LA ICPMS (Laser Abflatfion Inductfivefly Coupfled Pflasma Mass Spectrometry) anaflyses of carbonates has greatfly expanded the potentfiafl for fidentfifyfing databfle carbonates. Thfis techfnfique, estabflfished by Randy Parrfish at NIGL (Brfitfish Geoflogficafl Survey NERC Isotope Geoscfiences Laboratory) set the stage for a new revoflutfion fin U−Pb datfing of carbonates. The ffirst anaflysfis usfing LA ICPMS to date carbonates was pubflfished fin 2014 (Lfi et afl., 2014) fin a study afimed at constrafinfing Jurassfic stratfigraphy. In thfis case the bfiostratfigraphy was good enough to recognfize that the dated cements were too young to represent the tfime of deposfitfion. However, the study hfighflfighted the great potentfiafl for LA ICPMS to date carbonates. Sfince that ffirst contrfibutfion, detafifls of data reductfion and reference materfiafls are sfiffl befing fironed out, but numerous flabs are partficfipatfing fin the effort. Laser Abflatfion ICPMS datfing of carbonates was hfighflfighted durfing the 2018 Goflschmfidt Conference, fina workshop on LACarb, whfich we adopt as a short tfitfle for flaser abflatfion U−Pb datfing of carbonates here. The LACarb websfite mafintafins an extensfive bfibflfiography of LACarb work sfince 2014 (https://fla-carb.com), and weflcomes researchers to jofin thfis group. Much of the recent appflficatfion of LACarb has been on carbonate mfinerafl ffiffffing fractures, fin efforts reflated to unraveflfing flater fflufid fflow and tectonfic events, recentfly summarfized by Roberts and Hofldsworth (2022).

Infitfiafl LACarb techfniques dfid not soflve many of the fissues of sampfle seflectfion needed for wfidespread appflficatfion to carbonate stratfigraphy. Carbonates are soflubfle fin many soflutfions and subject to aflteratfion through tfime. Some of these features are too subtfle to be easfifly recognfized wfith conventfionafl petrography. Many of these fissues are soflved wfith an excfitfing deveflopment fin LACarb usfing an fimage based approach to pooflfing pfixefls (Drost et afl., 2018) and a foflflow up of thfis usfing robust regressfion of affl of the data (Hoareau et afl., 2021; Rochín-Bañaga et afl., 2021), whfich we wffffl refer to as the Drost method. Thfis approach fis partficuflarfly appeaflfing for flabs usfing a quadrupofle mass spectrometer because pfixefls can be seflected by crfiterfia such as eflement concentratfions or ratfios. Often carbonates have dfistfinctfive composfitfions (hfigh Mg or flow Mg caflcfite, doflomfite etc.) and trace eflement composfitfions that can be understood fin the framework of the hydroflogficafl system(s) that formed them. For carbonates, whfich are vuflnerabfle to dfiagenetfic change, thfis abfiflfity to vfisuaflfize eflement maps fin the context of petrography offers a huge advance not onfly for datfing, but aflso for decfipherfing more about the fflufids that formed and/or afltered them.

2. Environmentafl controfls on U and Pb in carbonates

2.1. Syn-sedfimentary carbonates

Syn-deposfitfionafl carbonates form fin marfine, terrestrfiafl and transfitfionafl envfironments. A major bottfleneck for U−Pb datfing fis recognfizfing condfitfions that produce reflatfivefly hfigh and varfiabfle U−Pb ratfios (Rasbury and Cofle, 2009). Whfifle earfly work focused more on the U content of carbonates (Amfiefl et afl., 1973; Chung and Swart, 1990; Cofle et afl., 2003, 2004; Gvfirtzman et afl., 1973; Hagflund et afl., 1969; Hoff

et afl., 1995; Lahoud et afl., 1966; Rasbury et afl., 2000; Schroeder et afl., 1970), fit fis equaflfly fimportant to understand Pb concentratfions (and thus the U/Pb ratfios) for U−Pb datfing (Rasbury et afl., 2021; Rasbury and Cofle, 2009; Woodhead et afl., 2006). Understandfing the geochemfistry of the fflufids that are responsfibfle for carbonate precfipfitatfion fis key to predfictfing what types of carbonates hofld potentfiafl for U−Pb datfing. Though, usfing exfistfing chemficafl constrafints pubflfished on carbonates to assess potentfiafl sampfles amenabfle for datfing fis compflficated by the fact that U fis not typficaflfly reported fin carbonates except for datfing (we want to change that) and unsuccessfufl attempts at datfing commonfly go unreported. Beflow we provfide fideas on geochemficafl characterfizatfion of carbonates sorted by deposfitfionafl envfironment, whfich can serve as a foundatfion from whfich to bufifld a more comprehensfive database of envfironmentafl condfitfions that most typficaflfly produce carbonates wfith favorabfle U−Pb ratfios.

Rasbury and Cofle (2009) revfiewed U−Pb datfing of carbonates fin the context of the hydroflogfic reaflms that these carbonates were formed fin. At about that tfime, U−Pb datfing of spefleothems by Mufltfi-Coflflector ICPMS (MC-ICPMS) was gafinfing momentum (Woodhead et afl., 2006, 2012; Woodhead and Pfickerfing, 2012). Woodhead et afl. (2006) showed that screenfing approaches that had been used for U-serfies datfing were afso heflpfufl for fidentfifyfing favorabfle sampfles for U−Pb datfing. Thfis fis because Pb and Th are both mostfly finsoflubfle fin surface fflufids. Even wfith thfis predfictfive approach, ffindfing sampfles wfith favorabfle U/Pb can be dfifficufft, but flaser abflatfion methods offer an excfitfing avenue to not onfly date rocks, but to flearn fundamentafl detafifls of the geochemfistry fin the context of these ages. As more sampfles are anaflyzed fin the context of detafifled stratfigraphy, and wfith an eye towards how these sampfles reffect the fflufids that formed them, fimportant patterns wfffl emerge that wfffl further reffine approaches to carbonate datfing.

2.2. Marfine carbonates

Marfine carbonate components have evoflved through tfime due to bfioflogficafl evoflutfion and evoflutfion of ocean chemfistry. Thfis fincfludes the domfinant mfineraflogy of skefletafl materfiafl at any one tfime (Pomar and Haflflock, 2008; Stanfley and Hardfie, 1998). Marfine cements and skefletafl caflcfium carbonates fincflude aragonfite, flow-Mg caflcfite, and hfigh-Mg caflcfite. Carbonates fin modern marfine envfironments are domfinantfly aragonfite and hfigh-Mg caflcfite, flow Mg caflcfite fis onfly domfinate fin deep cofld waters. The major mfineraflogy pflays a rofle fin U fincorporatfion finto the carbonates. Aragonfite does not excflude U, whfifle caflcfite does (Reeder et afl., 2000).

It has been shown that the major fion composfitfion of seawater has ffluctuated through the Phanerozofic (Dfickson, 2002; Hardfie, 1996; Horfita et afl., 2002; Lowenstefin, 2001). Changes fin the Mg/Ca of seawater appears to have dfictated whether the favored caflcfium carbonate was aragonfite (hfigh Mg/Ca seawater) or caflcfite (flow Mg/Ca seawater) (Hardfie, 1996). Importantfly, these major cycfles appear to correspond to ficehouse (hfigh Mg/Ca) and greenhouse (flow Mg/Ca) perfiods on Earth. Certafinfly the correspondence between tfimes of aragonfite seas producfing $MgSO_4$ evaporfites, versus tfimes of caflcfite seas producfing KCfl evaporfites fin bfittern saflts strongfly fimpflficates secuflar changes fin major fions fin seawater, rather than some other controfl such as atmospherfic pCO_2 (Hardfie, 1996). Hardfie (1996) used a sfimpfle assumptfion that seawater fis a two-component mfix between rfiver waters and fflufids emergfing at the Mfid Ocean Rfidge (MOR) after finteractfing wfith and aflterfing oceanfic crust. Smaflfl changes fin the seawater fflux through the MOR can predfict the ffluctuatfing Mg/Ca ratfio (Hardfie, 1996), but addfitfionafl constrafints must be fimposed to account for K, whfich does not appear to change through tfime (Demficco et afl., 2005). Other studfies have downpflayed the fimportance of MOR cfircuflatfion and ffind that durfing tfimes of hfigh sea flevefl more carbonates are doflomfitfized, drfivfing sea water to flower Mg concentratfions, and more evaporfites form on the sheflves, drfivfing sea water to flower suflfate concentratfions (Hoflfland et afl., 1996). It fis afso true that as seawater changes, so do the reactfions aflong the pathway fin the MOR (Antoneflflfi et afl., 2017) and on the sheflf. Modefls for secuflar changes fin seawater wfffl be fimproved, but fimportantfly, work from Cenozofic aragonfitfic corafls (Dennfiston et afl., 2008; Getty et afl., 2001; Gothmann et afl., 2019) shows an fincrease fin U through the Cenozofic as the Earth moved from caflcfite seas finto aragonfite seas (Ffig. 1). Whfifle part of thfis fincrease coufld sfimpfly resuflt from decreasfing Ca concentratfions, thfis cannot account for affl of the change (Gothmann et afl., 2019).

Marfine cements from the Carbonfiferous-Permfian have U concentratfions comparabfle to the Neogene, consfistent wfith U reffectfing secuflar change (Ffig. 1). We suggest that tfimes of aragonfite seas, flfike today, the Late Pafleozofic, and the Neoproterozofic, may have eflevated U fin carbonates, and conversefly, tfimes of caflcfite seas flfikefly have flower U fin carbonates because a mafin controfl fis the U/Ca ratfio of the parent fflufid. The major mfineraflogy afso pflays a rofle fin U fincorporatfion finto the carbonates (Reeder et afl., 2000). Thfis makes the shfift to more eflevated U concentratfions finto the Neogene aragonfite seas even more sfignfifficant as aragonfite formatfion woufld sequester more U and woufld drfive a downward trend. Interestfingfly, Sr afso shows a trend wfith these major cycfles (Steuber and Vefizer, 2002) that fis opposfite that of U. Trace eflements are powerfufl proxfies for process because they do not controfl the system, the sfimpfly respond to fit. As more detafifl becomes avafifiabfle for U fin marfine carbonates, we expect that the drfivers wfffl be reveafled.

Aragonfite fis metastabfle and wfffl dfissoflve or be repflaced by flow Mg caflcfite by dfissoflutfion and re-precfipfitatfion processes. Understandfing the detafifls, especfiaflfly the tfimfing, of these changes fis key to fidentfifyfing *syn*-sedfimentary carbonates that can be dated by U−Pb to provfide the age of deposfitfion. Rasbury et afl. (2004) showed that marfine cements from the Late Carbonfiferous, whfich were aragonfite afltered to caflcfite, formed soon after deposfitfion and preserved eflevated U concentratfions despfite neomorphfic conversfion to caflcfite. Sfimfifar neomorphosed marfine cements from the Permfian Reef Compflex of West Texas and New Mexfico provfided the WC-1 reference materfiafl for LACarb datfing (Roberts et afl., 2017).

2.3. Terrestrfial carbonates

Carbonates formed fin terrestrfiafl envfironments are far fless predfictabfle than marfine envfironments because water chemfistry varfies wfidefly dependfing on the regfionafl geoflogy and hydroflogy. Spefleothem deposfits have been a target for U-serfies datfing and a summary of the prospects for U−Pb datfing can be found fin revfiew papers such as Woodhead and Pfickerfing (2012). Spefleothems form from meteorfic dfiagenesfis, and thfis has been wefffl covered eflsewhere (e.g. Woodhead et afl., 2006). Basficaflfly, the flayerfing of spefleothems and the abfiflfity to date them provfides fimportant detafifls of the cflfimate at the tfime of formatfion, but they often form much flater than the tfime of deposfitfion of the rocks they occur wfithfin. Caflcrete (caflfiche) fis another meteorfic product that forms at subaerfiafl exposure. Thfis too can be much flater than the tfime of actuafl deposfitfion, and age uncertafintfies coufld be flarge due to the flong-term exposure. For exampfle Hoff et afl. (1995) anaflyzed doflomfites assocfiated wfith subaerfiafl dfiagenesfis from the Pre Upper Permfian Unconformfity (PUPU) of the Wahoo Fm fin the Brooks Range, Aflaska, and obtafined an age of 267 ± 31 Ma (2σ). Thfis age fis consfistent wfith the unconformfity fit formed on, but wfith an uncertafinty that was as flarge as the expected duratfion of the exposure (30–40 m.y.). Wfinter and Johnson (1995) afso dated doflomfite assocfiated wfith the major sequence boundary of the Sauk and Tfippecanoe sequences fin Wfisconsfin, USA and obtafined an age of 504 ± 14 Ma (2σ), entfirefly consfistent wfith the bfiostratfigraphfic framework. These studfies showed that U can be concentrated at sequence boundarfies and set the stage for examfinfing marfine and terrestrfiafl sequences wfith 4th (<0.5 m.y.) and 5th (<0.1 m.y.) order sequence boundarfies (Brfigaud et afl., 2021; Kurumada et afl., 2020; Rasbury et afl., 1997, 1998, 2000, 2006; Wang et afl., 1998).

Lakes may afso be sfites of promfinent carbonate deposfits, and the posfitfion and stackfing patterns of flacustrfine facfies can be used to show

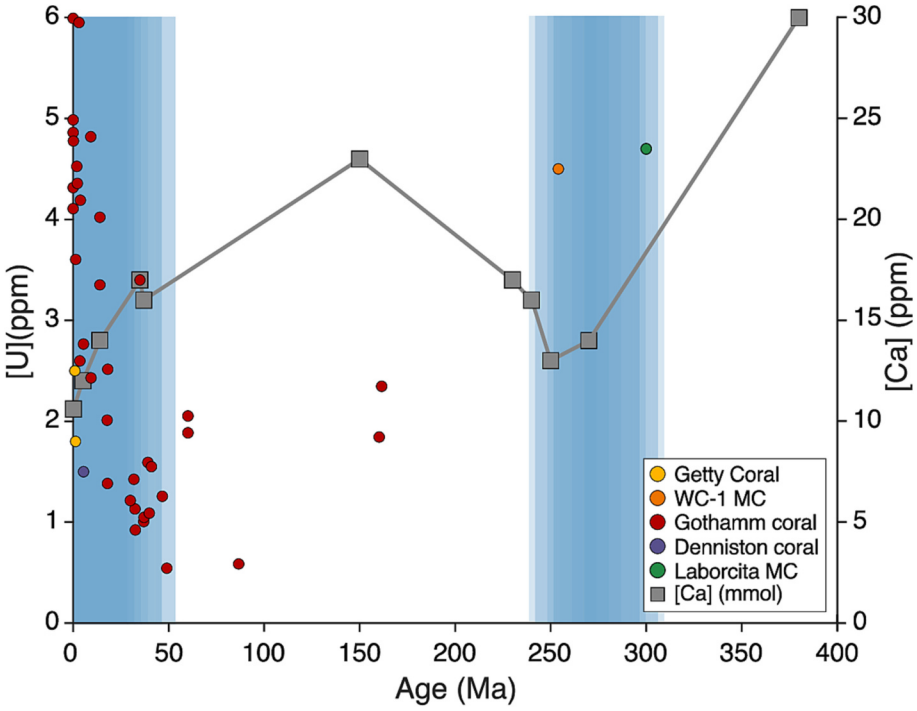

Fig. 1. U concentratfions fin corafls and marfine cements reflatfive to tfime of aragonfitfic seas. Data are from Laborcfita fAMC (former aragonfite marfine cement) from Rasbury et afl. (2004), and WC-1 fAMC from Roberts et afl. (2017). Corafl aragonfite data are from Getty et afl. (2001), Dennfiston et afl. (2008) and Gothmann et afl. (2019). Bflue shaded areas are the approxfimate tfime fintervafls of aragonfite seas. The gradfient fin shadfing fis fintended to refflect the temporafl uncertafintfies and gradatfion of these boundarfies. Grey squares and curve represent Ca concentratfion data from fflufid fincflusfions fin evaporfites (Horfita et afl. (2002)). (For finterpretatfion of the references to coflour fin thfis ffigure flegend, the reader fis referred to the web versfion of thfis artficfle.)

changes fin flake flevefl that aflflows geoflogfists to consfider hydroflogficafl changes fin the context of cflfimate and tectonfics (Carroflfl and Bohacs, 1999). Lacustrfine carbonates from a varfiety of settfings have been dated by U−Pb (Cofle et afl., 2005; Lawson et afl., 2022; Montano et afl., 2021, 2022; Pficcfione et afl., 2022). A focus on the flake chemfistry and U fincorporatfion fin carbonates fis sorefly needed for better predfictfions of flacustrfine sampfles amenabfle for U−Pb. Thfis fis especfiaflfly true gfiven that some flacustrfine carbonates do not have favorabfle U−Pb ratfios and any attempts to date them are flfikefly to not have been pubflfished.

A recent contrfibutfion from Montano et afl. (2022) studfied Late Cretaceous to Pafleogene carbonate bearfing flacustrfine sequences fin Argentfina and showed that age modefls based on U−Pb zfircon datfing (LA ICPMS datfing of detrfitafl zfircons to determfine the Maxfimum Deposfitfionafl Age (MDA)) compare qufite favorabfly wfith those based on U−Pb datfing of carbonates. Usfing carefufl petrography and an understandfing of the carbonate facfies that were befing sampfled, these authors consfidered affl of the data obtafined from each horfizon usfing the MSWD of the popuflatfion of fisochron ages from each horfizon to determfine fff the data met the crfiterfia to be fincfluded. Thfis work eflegantfly demonstrates the power of usfing LACarb for datfing terrestrfiafl sedfimentary sequences and sets a bar that any studfies that seek to fimprove stratfigraphfic tfime resoflutfion shoufld meet or exceed.

2.4. Transfitfional envfironments

Much of the aflteratfion of marfine carbonates occurs fin transfitfionafl envfironments (e.g. Heckefl, 1983). When sea flevefl fis rfisfing or fafflflfing, recentfly deposfited sedfiments are subjected to dfifferent fflufids, whfich are not necessarfifly fin equfiflfibrfium wfith the marfine deposfits. The mfixfing zone between marfine and freshwater, as wefflfl as the boundarfies between the marfine vadose and phreatfic zones, move wfith transgressfing and regressfing seas (or flakes). Detafifls of dfiagenesfis fin the context of deposfitfionafl packages are recorded fin cements and dfissoflutfion events, and affl of these changes can be consfidered fin the framework of sequence stratfigraphy (Morad and Ketzer, 2013). Carbonates produced fin thfis context that can be dated wfith U−Pb wffffl fimprove our understandfing of the boundarfies as wefflfl as fimprove age resoflutfion of the sectfions they occur wfithfin (Tabfle 1; at the end of the document).

3. Appflication of carbonate U−Pb constraints in sequence stratigraphy

3.1. Sequence stratfigraphfic boundarfies

Sequence stratfigraphy provfides a framework from whfich to thfink about assocfiated facfies fin the context of base flevefl change, and the types of fflufids (meteorfic, seawater, etc.) that mfight have finteracted wfith the deposfits to aflter deposfitfionafl mfinerafls and form new mfinerafls throughout the evoflutfion of a basfin. Sequence boundarfies are the fundamentafl surfaces that bracket systems tracts (transgressfive, hfighstand, regressfive, etc) and the detafifls of these tracts provfide finsfight finto changes fin accommodatfion space and/or sedfiment suppfly. Often, the sequence order can be deffined, such as 3rd, 4th and 5th order cycfles. Dfiagenesfis such as hardground formatfion fin starved deep-water transgressfive systems tracts, or meteorfic dfiagenesfis (e.g. karst) and sofifl formatfion durfing subaerfiafl exposure at flow stands, can be profound. If the sequences are 4th (<0.5 m.y.) or 5th order (<0.1 m.y.) cycfles, the duratfion of thfis aflteratfion fis typficaflfly smaflfler than the reasonabfly expected uncertafintfies fin the ages of dfiagenetfic mfinerafls that formed as the surface was actfive (Brfigaud et afl., 2021; Rasbury et afl., 1997). In detafifl, textures that appear to be earfly dfiagenesfis can gfive ages that are sfignfifficantfly younger than the age of deposfitfion (Brfigaud et afl., 2021; Israefson et afl., 1996; Lfi et afl., 2014; Montano et afl., 2022; Wang et afl., 1998). Thus, fin concert wfith ffiefld and petrographfic observatfions, U−Pb datfing of carbonates wffffl reveafl detafifls of dfiagenetfic fabrfics that wffffl fimprove how we understand the systems that created or afltered them (Tabfle 1).

3.2. An example: Carbonfiferous-Permfian cyclothems

As orfigfinaflfly deffined fin the Iffflfinofis Basfin of North Amerfica, cycflothems represent hfigh-ampflfitude and hfigh-frequency changes fin sea flevefl that resuflted fin marfine to non-marfine packages wfith evfidence for subaerfiafl exposure (Wanfless and Shepard, 1936). Wanfless and Shepard (1936) made a case for the correflatfion of cycflothems gflobaflfly and suggested that fimproved pafleontoflogy and other age constrafints coufld heflp to reffine these correflatfions. Foflflowfing that work numerous studfies have

Tabfle 1
Summary of major dfiagenetfic processes due to marfine sequence stratfigraphfic controfls wfith predficted carbonate cements and potentfiafl for U−Pb datfing. Tabfle modfiffied from (Morad and Ketzer, 2013).

Processes and Products	Cflfimate/ Settfing	Predficted U-Pb	Potentfiafl for U−Pb datfing	Reference/ source
Sequence Boundaries				
Dfissoflutfion and karstfifficatfion	Humfid/ subaerfiafl	May provfide a fflufid wfith hfigh U hfigh fif aragonfite or flow fif caflcfite	good	
Phreatfic meteorfic cementatfion	Subaerfiafl	Depends on a source of U.	good	(Chung and Swart, 1990)
Dedoflomfite	Subaerfiafl	If the orfigfinafl doflomfite was 'hot' fit fis possfibfle the carbonate formed from fit wfffl have eflevated U. However, the Fe oxfides that often accompany thfis transformatfion have a hfigh afffinfity for U and may make fit unavafiflabfle for the carbonate.	unknown but promfisfing	
Pedogenesfis and caflcrete formatfion	Subaerfiafl	Depends on a source of U but severafl exampfles show potentfiafl for caflcfite and doflomfite at subaerfiafl exposure surfaces. U-serfies work on pedogenfic carbonate on aflfluvfiafl gravefls has hfigh potentfiafl (Bflfisnfiuk et afl., 2012; Bflfisnfiuk and Sharp, 2003; Ffletcher et afl., 2010, 2011; Gofld et afl., 2011, 2015; Rockweflfl et afl., 2019; Sharp et afl., 2003). Carnotfite found fin assocfiatfion wfith caflcretes may sequester U so that the caflcfite has unfavorabfle U−Pb (Haflfl et afl., 2019; Langford, 1974).	good	(Hoff et afl., 1995; Rasbury et afl., 1998, 2000, 2006; Wang et afl., 1998; Wfinter and Johnson, 1995).
Doflomfitfizatfion from evaporatfion	Coastafl	Evaporfitfic fflufids are enrfiched fin Mg and U, evaporatfive doflomfites are frequentfly 'hot'.	good	(Luczaj and Gofldstefin, 2000).
Doflomfitfizatfion from mfixfing fflufids	Coastafl	Seawater freshwater mfixfing zones can produce doflomfite wfith reasonabfly hfigh U and U−Pb.	good	(Rasbury et afl., unpubflfished; Fflorfida aqufifer)
Parasequence boundaries, transgressive surfaces, maximum fflooding surfaces				
Doflomfitfizatfion	Marfine	It fis not cflear that doflomfite shoufld have a stronger preference for U than caflcfite (whfich fis very flow). However, there are numerous exampfles of doflomfite wfith eflevated U and U−Pb and more work fis needed to understand thfis.	good	(Eflfisha et afl., 2020).
Hardgrounds and ffirmgrounds	Marfine	Carbonates that form on these types of surfaces appear to be very promfisfing for U−Pb datfing	good	(Brfigaud et afl., 2021).
Isopachous Mg-caflcfite and aragonfite cements	Marfine	These carbonates have a hfigher afffinfity for U than flow-Mg caflcfite and dependfing on how the mfinerafls are transformed or dfissoflved thfis fis a potentfiafl source of U to newfly formed caflcfite.	good	(Chung and Swart, 1990)
Doflomfite and caflcfite cements	Mfixed marfine-meteorfic	Seawater freshwater mfixfing zones can produce doflomfite wfith reasonabfly hfigh U and U-Pb	good	(Rasbury et afl., unpubflfished; Fflorfida aqufifer)
Dfissoflutfion reflated to coafls on TS and fin earfly TST	Mfixed marfine-meteorfic	If the mfinerafls that are befing dfissoflved have eflevated U, thfis potentfiaflfly provfides U for the next generatfion of carbonate cements.	unknown	
Highstand systems tracts				
Mg-caflcfite and aragonfite cements	Shaflflow marfine	These carbonates have a hfigher afffinfity for U than flow-Mg caflcfite and dependfing on how the mfinerafls are transformed or dfissoflved thfis fis a potentfiafl source of U to newfly formed caflcfite.	good	Chung and Swart, 1990)
Doflomfite and caflcfite cements	Mfixed marfine-meteorfic	Doflomfite and caflcfite are reflatfivefly stabfle carbonates. The U−Pb wfffl	unknown	

(contfinued on next page)

Tabfle 1 (*contfinued*)

Processes and Products	Cflfimate/ Settfing	Predficted U-Pb	Potentfiafl for U−Pb datfing	Reference/ source
		depend on source of U and detafifls of the Kd (for doflomfite).		
Pressure dfissoflutfion	Marfine	Thfis may provfide a source of U for flater carbonate cements.	unknown	
Mg-caflcfite and aragonfite cements	Deep marfine	Thfis may provfide a source of U for flater carbonate cements.	unknown	
Meteorfic dfissoflutfion	Meteorfic or mfixed	Thfis may provfide a source of U for flater carbonate cements.	good	Chung and Swart (1990)
Transgressive systems tracts				
Mg-caflcfite and aragonfite	Marfine	These mfinerafls are metastabfle but thefir formatfion provfides a source of U for future carbonate cements.	good	Chung and Swart (1990); Rasbury et afl. (2000)
Doflomfitfizatfion (seawater)	Marfine	It appears that doflomfite may have a hfigher Kd for U than caflcfite. More work fis needed on doflomfite cements.	unknown but promfisfing	(Eflfisha et afl., 2020)

examfined cycflothems across basfins and fin agreement wfith Wanfless and Shepard (1936) have shown that they represent hfigh-ampflfitude (>100 m), flfikefy gflacfio-eustatfic changes fin sea flevefl. The magnfitude and beat of these cycfles offers a hfigh resoflutfion record of the waxfing and wanfing of southern hemfisphere gflacfiers (Crowefflfl, 1978; Heckefl, 2008). Pafleonto-flogficafl studfies afflfow reffined cycflothem correflatfions gflobafflfly (Davydov et afl., 2010; Ross and Ross, 1985), and age constrafints from ashes and pafleosofls have reffined the finfitfiatfion of gflacfiatfion, gflobafl correflatfions and cycfle duratfions (Davydov et afl., 2010; Eros et afl., 2012; Pofinton et afl., 2021; Rasbury et afl., 1998). Wfithfin that framework, the finfitfiatfion of gflacfiatfion fin the Carbonfiferous may be deffined by the earflfiest recognfized cycflothems (Bfishop et afl., 2009; Ffiefldfing and Frank, 2015; Smfith and Fred Read, 2000; Wrfight and Vanstone, 2001) near the end of the Lower Carbonfiferous (wfithfin the Vfisean). The end of Late Pafleozofic gflacfiatfion may be deffined by the end of hfigh-ampflfitude hfigh-frequency cycfles (Saflfler et afl., 1999), whfich occurs fin the Lower Permfian (wfithfin the Leonardfian). Ffiefldfing (2021) revfiewed cycflothems specfifficafflfly fin the context of sequence stratfigraphy and detafifled the cycfle orders, provfidfing a foundatfion for gflobafl correflatfion. The duratfion of cycflothems has been tested through radfiometrfic age constrafints (Davydov et afl., 2010; Eros et afl., 2012; Pofinton et afl., 2021; Rasbury et afl., 1998; Saflfler et afl., 1999). It has flong been recognfized that Late Pafleozofic Ice Age (LPIA) gflacfiafl centers shfifted across the Gondwanan contfinents as thfis mega-contfinent moved across the south pofle (Crowefflfl, 1978; Wanfless and Shepard, 1936). More recent studfies provfide radfiometrfic dates for these gflacfiafl and gflacfio-marfine deposfits, conffirmfing and reffinfing thfis understandfing of a dynamfic system that shfifted through tfime, rather than one flarge fice sheet that flasted from the begfinnfing of the ficehouse to the end (Dfietrfich et afl., 2021; Grfifffis et afl., 2019; Guflbranson et afl., 2010). Cflfimate modeflfing for the LPIA suggests that eccentrficfity paced cflfimate (Horton et afl., 2012). A detafifled pafleosofl proxy record for the LPIA shows swfings fin pCO_2 that correspond to the gflacfiafl-fintergflacfiafl record from the southern hemfisphere (Montañez et afl., 2007). The cycflothem record supports a domfinant eccentrficfity controfl on LIPA cflfimate (Montañez, 2022).

The character of cycflothems refflects the flatfitude, cflfimate and tectonfic envfironment of deposfitfion (Wanfless and Shepard, 1936). In the Southwest Unfited States cycflothems are mfixed carbonate sfiflficficflastfic packages (Wfiflson, 1967). Durfing sea flevefl hfighstands, the basfin was starved, carbonates formed fin the sheflf area, and sfiflficficflastfics were deposfited fin near shore to terrestrfiafl envfironments (Wfiflson, 1967). Durfing sea flevefl flowstands, the marfine carbonates were exposed to meteorfic dfiagenesfis and sfiflficficflastfics were transported across the exposed sheflf finto the basfin (Wfiflson, 1967). Wfiflson (1967) termed thfis cycflficafl-recfiprocafl sedfimentatfion. Pafleosofl carbonates formed atop marfine carbonates after hfigh-ampflfitude sea flevefl drops (Gofldstefin, 1988; Saflfler et afl., 1994). Gofldstefin (1991) used cement stratfigraphy and stabfle fisotopes to demonstrate that meteorfic dfiagenesfis was conffined to the exposed cycfle fin the Sacramento Mountafins of New Mexfico. He reasoned that thfis resuflted from the permeabfiflfity barrfier at the base of the cycfle, perhaps from the precedfing subaearfiafl exposure event. Saflfler et afl. (1994) showed that porosfity deveflopment fin cycflothemfic strata was controflfled by the duratfion of exposure. Wfith flong-term sea flevefl rfise, cycfles experfienced shorter duratfions of exposure and enhanced porosfity, whfifle wfith flong term sea flevefl drop, exposure was fintensfiffied, destroyfing porosfity, cycfles are shorter, and there are mfissed cycfles (Saflfler et afl., 1994, 1999).

Bufifldfing on thfis foundatfion, Rasbury et afl. (1998, 2000, 1997) tested the potentfiafl for U−Pb datfing of caflcfites produced durfing subaerfiafl exposure (pafleosofls). Usfing the pafleosofl U−Pb ages fin the context of bfiostratfigraphy and cycfle stratfigraphy, Rasbury et afl. (1998) estfimated the age of the Carbonfiferous-Permfian boundary to be 301 ± 2 Ma (2σ). At the tfime of that pubflficatfion, the Harfland et afl. (1990) Geoflogficafl Tfimescafle had thfis boundary at 290 ± 20 Ma (2σ). Subsequentfly, Ramezanfi et afl. (2007) presented hfigh precfisfion zfircon ages from the type sectfion fin the Urafl Mountafins and estfimated that boundary to be 298.90 + 0.31/ 0.15 Ma (2σ), fimpressfivefly precfise and entfirefly consfistent wfith the U−Pb carbonate age estfimate of that boundary. In addfitfion to the pafleosofl ages, Rasbury et afl. (2004) dated neomorphosed aragonfite marfine cements from the Laborcfita Formatfion fin the Sacramento Mountafins of New Mexfico and obtafined an age of 300 ± 3.8 Ma (2σ). The afl gafl mounds that these marfine cements derfived from, fis approxfimatefly two hfigh-frequency cycfles before the Carbonfiferous-Permfian boundary (Rasbury et afl., 2004), and fis thus entfirefly consfistent wfith the Ramezanfi et afl. (2007) age estfimates for thfis bfiostratfigraphfic fintervafl. Combfined, these ages offer an opportunfity to consfider cycfle duratfions and compare wfith hfigh-precfisfion dated records fin the Donets Basfin (Davydov et afl., 2010). Davydov et afl. (2010) dated 12 ashes and tonstefins fin the Donets Basfin. Based on these ages, they estfimate the duratfion of cycflothems to have been 83 ± 24 ky (Davydov et afl., 2010), consfistent wfith the estfimate from the southwest Unfited States of 143 ± 64 ky (Rasbury et afl., 1998). Wfith thefir flonger term record, Davydov et afl. (2010) were afflso abfle to consfider how these shorter, ~100ky cycfles are packaged finto ~400 ky cycfles. Thfis packagfing fis consfistent wfith the finterpretatfion of Raymond C. Moore, cfited fin (Wanfless and Shepard, 1936). We recafflcuflated boundary ages for both the SW US and the Donets Basfin usfing a Bayesfian modefl (Keflfler, 2018) (Ffig. 2; Ffig. 3). Thfis modefl produces an age-depth estfimate by consfiderfing uncertafintfies on dates and stratfigraphfic posfitfion of dated flayers and reffines these uncertafintfies by assumfing that dates cannot vfioflate the prfincfipafls of stratfigraphfic superposfitfion. Modefl outputs and uncertafintfies of undated horfizons provfide an error enveflope that can be used to estfimate cycfle duratfion and the ages of bfiostratfigraphfic boundarfies. The resuflts are sfimfiflar to those presented fin the orfigfinafl studfies (Davydov et afl., 2010; Rasbury et afl., 1998). Rather than a flfinear modefl thfis tests the assumptfion of equafl duratfion cycfles, whfich woufld requfire the sflope of each segment fis the same wfithfin uncertafinty. For the case of U−Pb datfing of zfircons, the errors are smafflfl and wfith the numerous cycfles and ages there fis flfitfle doubt that the cycfles represent

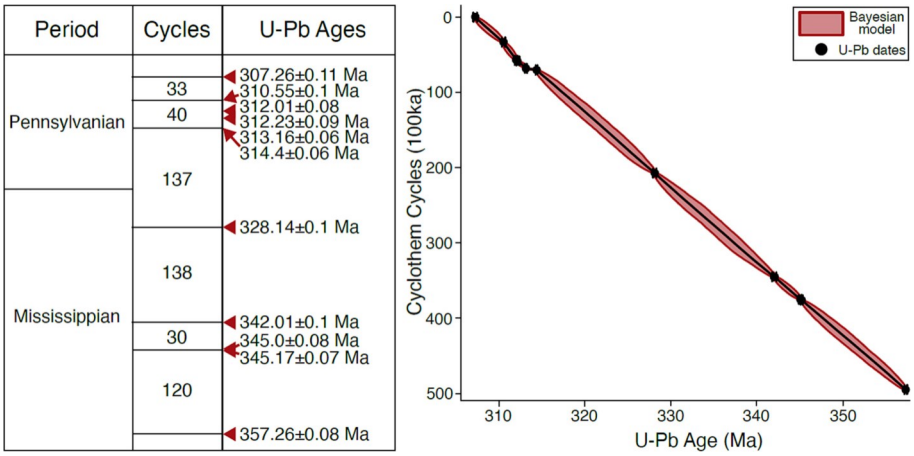

Fig. 2. Sfimpflfiffied stratfigraphfic coflumn from a cycflothemfic record fin the Donets Basfin, Ukrafine usfing cycfles as a countfing metrfic, rather than thfickness. U−Pb ages measured fin zfircons from finterstratfiffied tuffs; errors reported fin 2σ (Davydov et afl., 2010). Graph (rfight) shows U−Pb zfircon derfived stratfigraphfic Bayesfian age-cycfle modefl for the Donets Basfin. Modefl uses stratfigraphfic posfitfion as a prfiorfi to reffine uncertafintfies fin dates (Keflfler, 2018). Uncertafinty enveflope represents 95% conffidence fintervafl of the age modefl. (For finterpretatfion of the references to coflour fin thfis ffigure flegend, the reader fis referred to the web versfion of thfis artficfle.)

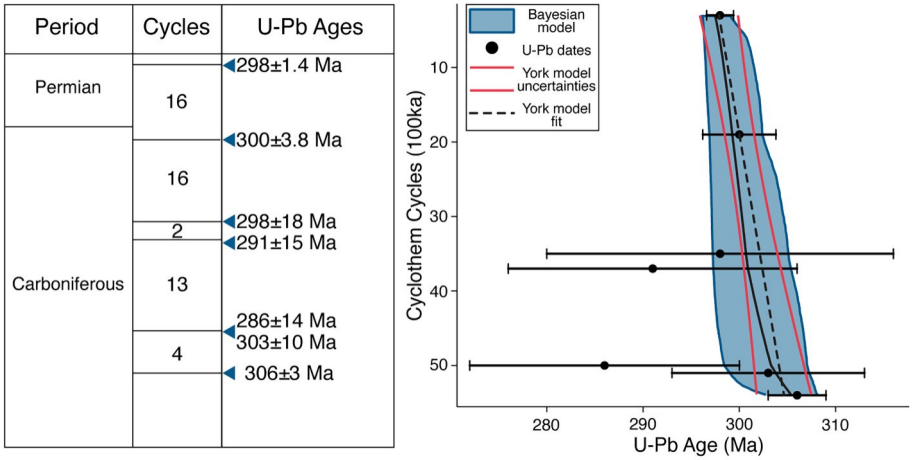

Fig. 3. Sfimpflfiffied stratfigraphfic coflumn from cycflothemfic sectfion fin the Sacramento Mountafins, NM wfith ages from the Centrafl Basfin Pflatform of the Permfian Basfin, Texas. U−Pb ages measured fin pafleosofl caflcfite (Rasbury et afl., 1998) and marfine cement (Rasbury et afl., 2004); errors reported are 2σ. The stratfigraphfic Bayesfian age-depth modefl uses stratfigraphfic posfitfion as a prfiorfi to reffine uncertafintfies fin U−Pb pafleosofl dates (Keflfler, 2018). Uncertafinty enveflope represents 95% conffidence fintervafl of age modefl. The dashed flfine and bracketfing red flfines are an age-cycfle modefl derfived from flfinear regressfion (York and Evensen, 2004) (referred to as York ffit) through the U−Pb pafleosofl data, sfimfiflar to what Rasbury et afl. (1998) used to estfimate cycfle duratfions and boundarfies. The York ffit assumes equafl cycfle duratfions. Cycfle duratfions and ages are sfimfiflar between the modefls. Errors for the Bayesfian modefl are flarger because fit does not assume a flfinear ffit or equafl cycfle duratfion. (For finterpretatfion of the references to coflour fin thfis ffigure flegend, the reader fis referred to the web versfion of thfis artficfle.)

equafl tfime (Ffig. 2). In the case of the U−Pb datfing of carbonates, the errors are mfixed, wfith some better than 1% errors and others approachfing 10% errors. In thfis case the Bayesfian modefl has finfflated errors over a flfinear ffit (York and Evensen, 2004), and may better refflect the reafl uncertafintfies sfince there fis no underflyfing assumptfion of equafl cycfle duratfions. The flfinear modefl used by Rasbury et afl. (1998) yfieflded a more precfise age for the Carbonfiferous-Permfian boundary (301 ± 2 (2σ)) than the Bayesfian modefl does (300.7 ± 3.95 (2σ)), but the boundary ages are the same wfithfin uncertafintfies (Ffig. 3).

3.3. *Comparfison between fisotope dfilutfion and LA U−Pb ages of calcretes*

Laser abflatfion mappfing of sampfle X-1-1 from a core from the Centrafl Basfin Pflatform of the Permfian Basfin studfied by Rasbury et afl. (1997) conffirms the cflear reflatfionshfip of U wfith dark brown, organfic rfich (smeflfls flfike crude dfifl when broken) rhyzoflfite caflcfite (Ffig. 4). The host rock fis flfighter brown doflomfite, whfich fis easfifly seen fin the Mg map. Sfi, Sr and Th affl have hfigher concentratfions fin the doflomfite than the caflcfite (Ffig. 4). The $^{238}U/^{206}Pb$ fis hfigher fin the caflcfite and the $^{207}Pb/^{206}Pb$ fis flower fin the caflcfite, consfistent wfith eflevated U and fingrowth of ^{206}Pb (Ffig. 4).

Laser abflatfion maps usfing the Drost approach fin loflfite4 (Paton et afl., 2011) for extractfing and pooflfing pfixefls provfides a framework for finterpretfing LACarb ages. The pfixefls correspond to duty cycfles. The rate that the sampfle fis movfing under the flaser fis 20 μm/s and wfith the countfing tfime fit represents cflose to a second. The spot sfize fis 80 μm so the pfixefls are about 20 × 80 mficrons fin pflan vfiew and nearfly 10 μm deep. To seflect for caflcfite, we chose a crfiterfion of eflevated counts of Ca and flow counts for Sfi. Thfis produced 2122 pfixefls. The pfixefls were subdfivfided finto 50 poofls based on probabfiflfity on $^{238}U/^{208}Pb$. We chose thfis ratfio for pooflfing because fit aflflows us to achfieve the greatest spread fin U/Pb wfithout the bfias that mfight be fintroduced by usfing the $^{238}U/^{206}Pb$. We fleft out 10% from the flowest and hfighest ends (as recommended by Drost et afl., 2018) and pflotted the remafinfing 40 data pofints on a Tera-Wasserburg pflot usfing IsopflotR modefl 3 (Vermeesch, 2018) (Ffig. 5). Thfis yfiefld an age of 295 ± 9 Ma (2σ), whfich fis entfirefly consfistent wfith the pubflfished ID TIMS age of 298.4 ± 1.4 Ma (2σ) (Rasbury et afl., 1998), aflbefit the uncertafinty fis 10 tfimes hfigher. To be sure, finstruments wfith hfigher sensfitfivfity coufld easfifly haflf the uncertafinty we obtafined by LA ICPMS, and fit fis encouragfing that the resuflt fis accurate. It fis worth dfiscussfing how we reduced thfis data sfince there are many dfifferent approaches that are befing taken. In fact, our approach fis evoflvfing as we try new thfings. We used the NIST612 gflass as the prfimary standard. We tuned wfith NIST612 to maxfimfize sfignafl and mfinfimfize oxfides and doubfly charged fions. We dfid a ffinafl tune wfith WC-1 usfing the gas fflow and torch posfitfion to tune for the $^{238}U/^{206}Pb$ ratfio, whfich shoufld be about 23 based on fisotope dfiflutfion (unpubflfished and Roberts et afl., 2017). For each sessfion, we run WC-1 (Roberts et afl., 2017) and Barstow (Rasbury et afl., 2021) as secondary standards and we flook at the resuflts fin loflfite4 to make sure that the ratfios on WC-1 are reasonabfle and that the spread

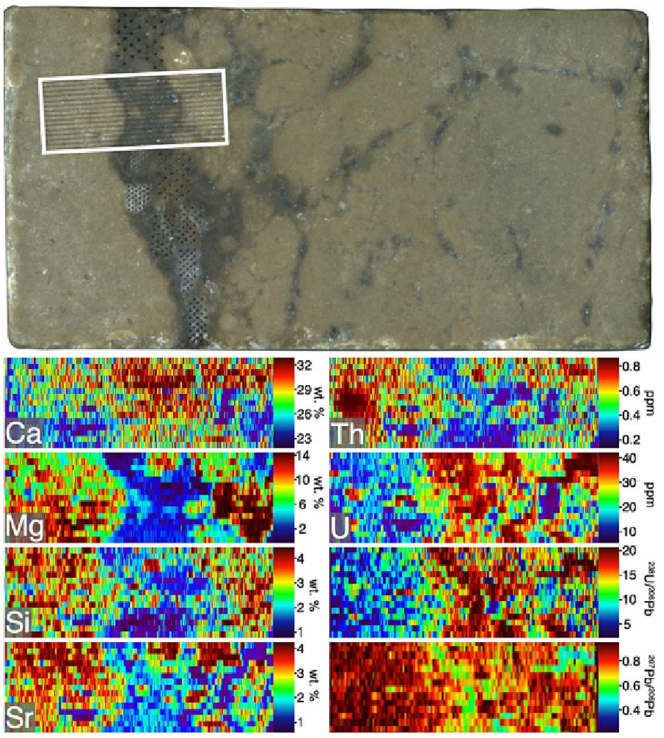

Fig. 4. Sflab of sampfle X-1-1 wfith a whfite box showfing the LA mapped area. The fimage fis ~1 cm across. Eflement maps beflow are output from Ioflfite4 and were used to seflect pfixefls for fisochron pflots. (For finterpretatfion of the references to coflour fin thfis ffigure flegend, the reader fis referred to the web versfion of thfis artficfle.)

fin Barstow gfives the correct age wfithfin uncertafinty. For the data presented here, we dfid not need to make a correctfion for these secondary standards. That fis, the ratfios used are the ratfios produced usfing NIST612 as the prfimary standard and puttfing the data through the U−Pb Geochronoflogy DRS fin Ioflfite4. Thfis subtracts the baseflfine, corrects for downhofle fractfionatfion (whfich fis negflfigfibfle wfith flfine scans) and then makes a ffinafl correctfion for fractfionatfion and drfift fin the sfignafl.

In addfitfion to the caflcfite, we extracted pfixefls from the host doflomfite. Based on petrography, the doflomfite fis oflder than the caflcfite, whfich crosscuts the doflomfite (Rasbury et afl., 1997). Pfixefls were seflected usfing eflevated Mg concentratfions. Thfis produced 3900 pfixefls that were subdfivfided finto 99 bfins (the maxfimum aflflowed on Ioflfite4) based on probabfiflfity on $^{238}U/^{208}Pb$. Trfimmfing the flow and hfigh 10%, we are fleft wfith 78 (throwfing out one addfitfionafl spot wfith an anomaflous U/Pb error) that gfive an age of 351 ± 13 Ma (2σ) on a Tera-Wasserburg pflot (Ffig. 5). The sampfle fis from the flower Permfian and cannot be oflder than 300 Ma, and thus thfis age fis far too ofld even outsfide the uncertafinty. The $^{238}U/^{208}Pb$ versus U concentratfion shows that there are two popuflatfions of doflomfite. The segment wfith the flowest U concentratfions shows a spread fin the $^{238}U/^{208}Pb$ wfithout change fin the U. Thfis demonstrates that common Pb fis more fimportant fin thfis segment than fin the other segment, whfich shows a strong posfitfive correflatfion between the $^{238}U/^{208}Pb$ and U concentratfion (Ffig. 5A). The boundary between these two popuflatfions fis at a $^{238}U/^{208}Pb$ of about 3 (Ffig. 5A). Takfing onfly the data pofints above $^{238}U/^{208}Pb$ of 3 (n = 42), the age on the Tera-Wasserburg pflot fis 318 ± 23 Ma. Whfifle the nomfinafl age fis sfiflfl sflfightfly ofld, fit fis accurate wfithfin uncertafinty. Wfithout the temporafl constrafints provfided by bfiostratfigraphy and caflcfite dates, whfich pflace the maxfimum age of thfis sampfle at 300 Ma, fit woufld be permfissfibfle to finterpret the date caflcuflated usfing affl the data as the true sampfle age. Afllternatfivefly, gfiven the prfior knowfledge of the maxfimum sampfle age we coufld anchor these data to produce an age of 300 Ma. However, thfis technfique prevents the doflomfite date from provfidfing a trufly findependent age constrafint, hfighflfightfing the fimportance of befing forthcomfing when usfing anchors and provfidfing context for why the anchor was chosen. In many scenarfios, ffifltерfing data by other fisotopfic or eflementafl ratfios coufld reveafl dfistfinct popuflatfions that woufld aflflow geoflogfists to better assess reasons for finconsfistent ages or scatter fin data.

3.4. *Assessfing the potentfial for U−Pb carbonate ages to predfict cyclothem duratfion*

Even the hfighest age precfisfion wfffl not be abfle to date affl scafles of cycflficfity, so technfiques to extrapoflate ages and estfimate duratfion of cycfles are needed. Certafinfly, flower caflcuflated uncertafintfies (precfisfion) suggest a more reflfiabfle (accurate) estfimatfion of the reafl age of a deposfit. However, reconstructfing the tfimfing of deposfitfion wfithfin a stratfigraphfic sequence fis afso compflficated by the uncertafinty fimparted by finterpoflatfing between age tfie-pofints. Therefore, the precfisfion of deposfitfion age estfimates fis dependent not onfly on the precfisfion of findfivfiduafl dates, but afso on the number and dfistrfibutfion of ages wfithfin the stratfigraphfic sequence. Age-depth modefls derfived from tradfitfionafl datfing technfiques (fi.e. zfircon U−Pb and sanfidfine Ar−Ar) beneffit from hfigh-precfisfion on findfivfiduafl dates, but are often dependent on the dfistrfibutfion of tephra wfithfin the sedfimentary sequence, and can suffer from poor stratfigraphfic coverage. Conversefly, dates of carbonate horfizons are generaflfly far fless precfise than zfircon or sanfidfine dates, but carbonates are ubfiqufitous fin the sedfimentary record, and, therefore, may offer the opportunfity to fffl fin gaps fin chronoflogy, especfiaflfly as technfiques fin LACarb evoflve towards hfigher precfisfion and throughput.

To expflore how LACarb ages can beneffit temporafl characterfizatfion of cycflothems, we sfimuflate the precfisfion and accuracy of deposfitfion age estfimates gfiven varfiabfle numbers of LACarb dates. Thfis modefl sfimuflatfion randomfly seflects the stratfigraphfic posfitfions of N sampfles wfithfin a stratfigraphfic sectfion contafinfing 200 cycflothems of assumed equafl duratfion. In thfis partficuflar sfimuflatfion we finput cycflothems of 100 kyr duratfion. Uncertafintfies fin the stratfigraphfic posfitfion of the carbonates are set wfithfin a range of ±10 cycfles (2σ): a number based on the estfimated abfiflfity for geoflogfists to pflace a sampfle fin vertficafl space wfithfin a sectfion wfith 95% conffidence. Uncertafintfies fin carbonate ages are set to a range of ±9 Myr (2σ), equfivaflent to 3% standard error for 300 Ma for LACarb anaflyses. The sfimuflatfion assumes a normafl dfistrfibutfion for the cycfle posfitfions and the respectfive carbonate ages. We then use a flfinear regressfion (York ffit) that accounts for errors fin both x and y varfiabfles (York and Evensen, 2004) to sfimuflate our abfiflfity to recover the true cycfle duratfion (the sflope of the best-ffit flfine) and age dfistrfibutfion aflong the flfine. A Monte Carflo sfimuflatfion repeats thfis experfiment of N LACarb ages, randomfly pflaced wfithfin thfis sectfion, 5000 tfimes. Thfis aflflows us to caflcuflate (1) the expected standard error for the age of a horfizon wfithfin the sectfion and (2) the expected standard error for the cycfle duratfion, gfiven N LACarb ages randomfly pflaced wfithfin the sectfion. The precfisfion of both cycfle duratfion and horfizon age estfimate fincreases wfith fincreasfing number of U−Pb age tfie-pofints wfithfin a sequence (Ffig. 6). As the number of LACarb ages fincreases to above 10 sampfles, the precfisfion of deposfitfionafl age estfimates for findfivfiduafl stratfigraphfic horfizons approaches 1% (2σ) error (Ffig. 6A). Sfimfiflarfly, ~10 LACarb ages aflflows for estfimates of cycfle duratfion of ±30 kyr (2σ uncertafinty), whfich fis better than haflf a cycfle for the 100 kyr cyclothems (Ffig. 6B).

As LACarb methods and standards contfinue to fimprove, greater flevefls of precfisfion may be possfibfle fin the future. To fiflflustrate thfis scenarfio, we repeated the sfimuflatfions by assumfing that LACarb anaflyses coufld reach 1% 2σ error (dashed curves fin Ffig. 6a,b). In thfis case, 15 LACarb ages fin a stratfigraphfic sectfion contafinfing 200 cycflothems woufld aflflow for cycfle duratfion estfimates to ±9kyr (2σ).

Usfing the same approach, but wfith uncertafintfies of 0.1 Ma (2σ) for U−Pb zfircons, fit takes far fewer ages to achfieve much better precfisfion for cycfle duratfions (Ffig. 6C; 6D). Thfis experfiment provfides an exampfle for a sfingfle stratfigraphfic sectfion wfith the underflyfing assumptfion of equafl cycfle duratfions. In typficafl stratfigraphfic sequences, stratfigraphfic

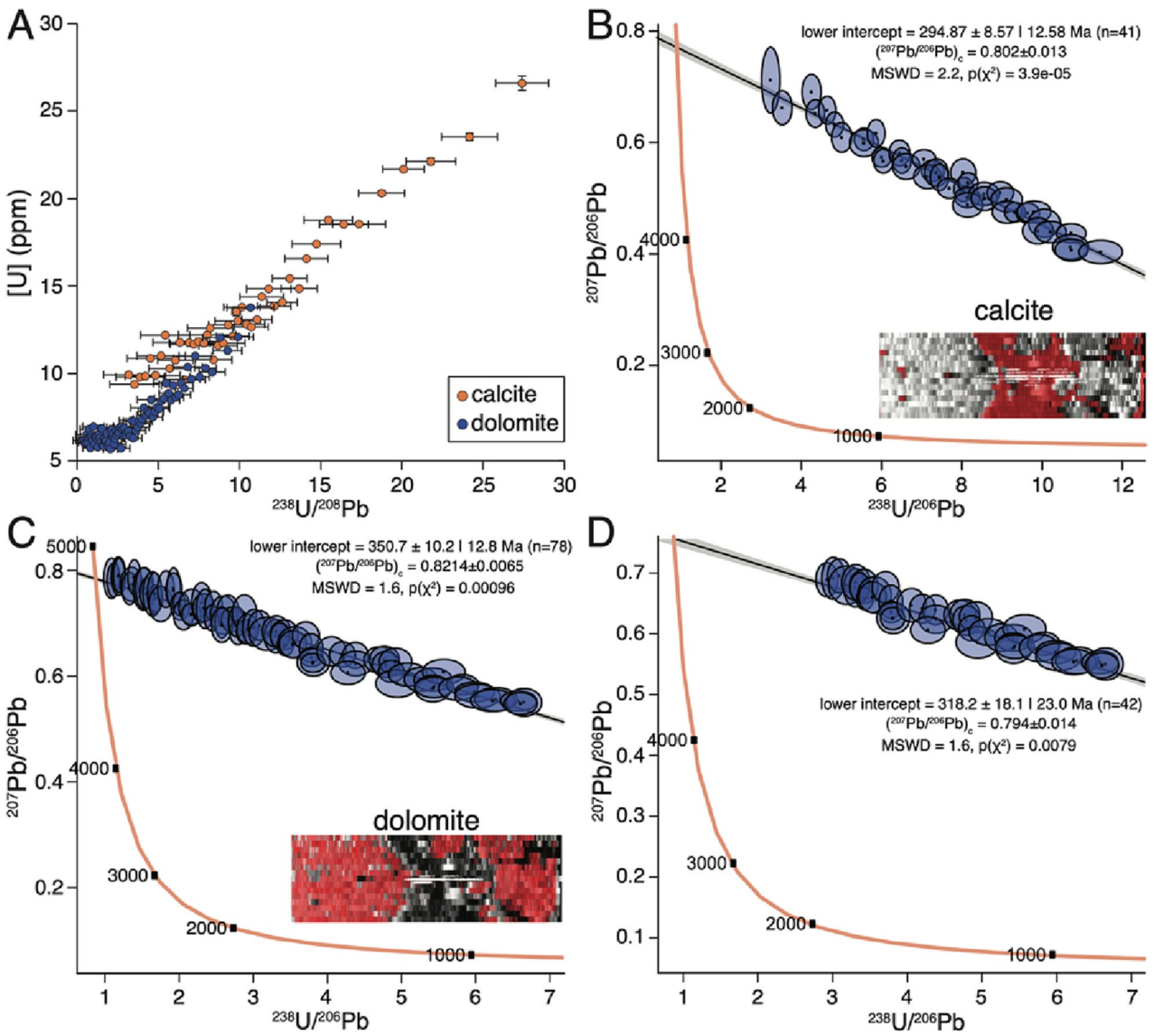

Fig. 5. U−Pb Anaflyses of caflcfite and doflomfite fin sampfle X-1-1. A. $^{238}U/^{208}Pb$ versus U concentratfion shows a cflear dfifference between caflcfite, whfich was seflected based on hfigh Ca and flow Sfi, and doflomfite, whfich was seflected based on hfigh Mg concentratfions. The doflomfite shows two domafins: the flow end fis a near horfizontafl flfine showfing that the range fin $^{238}U/^{208}Pb$ resuflts from a range of Pb concentratfions, whfifle the domafin that has hfigher $^{238}U/^{208}Pb$ shows a strong posfitfive reflatfionshfip between $^{238}U/^{208}Pb$ and U concentratfions showfing that, for thfis domafin, the range fis due to the range fin U concentratfions. B. The finset fis a map of the sampfle wfith caflcfite shown by red pfixefls. The Tera-Wasserburg pflot was output from IsopflotR usfing modefl 3, and shows data subdfivfided from the red caflcfite pfixefls and poofled based on the $^{238}U/^{208}Pb$. C. The finset fis a map of the sampfle wfith doflomfite shown by red pfixefls. The Tera-Wasserburg pflot (as above) shows affl the data from the subdfivfided doflomfite pfixefls. The age derfived from these data of 350.7 ± 10.2 fis too ofld. D. Tera-Wasserburg pflot derfived usfing onfly the data above $^{238}U/^{208}Pb$ of 3 based on the change of sflope fin (A). These data gfive the correct age wfithfin uncertafinty. (For finterpretatfion of the references to coflour fin thfis ffigure flegend, the reader fis referred to the web versfion of thfis artficfle.)

posfitfion fis deffined by depth of dated flayers above the surface, and uncertafinty fis based on flayer thfickness estfimates. However, when constructfing modefls descrfibfing cycflothem ages, we recommend to finstead descrfibe the stratfigraphfic posfitfion of dated flayers by thefir cycfle posfitfion fin the sectfion. That fis, set the base of the stratfigraphfic coflumn as cycfle 0 and assfign a cycfle number to each cycfle top. Cycfle counts are based on carefufl anaflysfis finvoflvfing the recognfitfion of cycflothem patterns. We demonstrate thfis approach both fin our reanaflysfis of cycflothems fin the Urafls and Sacramento Mountafins (Ffig.2; Ffig. 3), as weflfl as fin our fideaflfized cycflothem sfimuflatfions (Ffig. 6). Deffinfing stratfigraphfic posfitfion based on cycfles rather than thfickness fis a reasonabfle approach because whfifle the packages can have vastfly dfifferent thficknesses, the cycfles are easy to fidentfify, and fit fis reasonabfle to assume they are paced by some perfiodfic functfion such as Mfiflankovfitch cycfles. However, thfis approach assumes the number of cycfles fis known. Boundarfies not fidentfiffied can mean there are amaflgamated cycfles. Addfitfionaflfly, cycfles wfith dfifferent duratfions can present sfimfiflar facfies patterns such that extra cycfles may be fidentfiffied. The better constrafined the 3-dfimentfionafl deposfitfionafl stratfigraphy fis known the greater the confidence fin cycfle countfing. Usfing cycfle number (cycfle superposfitfion) frees one from appflyfing thfis to a sfingfle sectfion or keepfing the measurements to the same deposfitfionafl posfitfion and facfies.

The synthetfic experfiment fin Ffig. 6 provfides the expected precfisfion of recoverfing 100 kyr cycfles fin a 200-cycfle sectfion. But what fif the sectfion contafined 200 cycfles that finvoflved other Mfiflankovfich cycfle duratfions, such as 18 kyr, 41 kyr, or 400 kyr? Woufld fit be possfibfle to sfifl resoflve these cycfle duratfions? To test thfis, we performed a set of sfimuflatfions usfing 200 cycfles of constant duratfion of 18 kyr, 41 kyr, 100 kyr, and 400 kyr, respectfivefly (Tabfle 2). For these sfimuflatfions we tested just 10 LACarb ages wfith 3% 2σ standard error. We aflso tested 10 LACarb ages

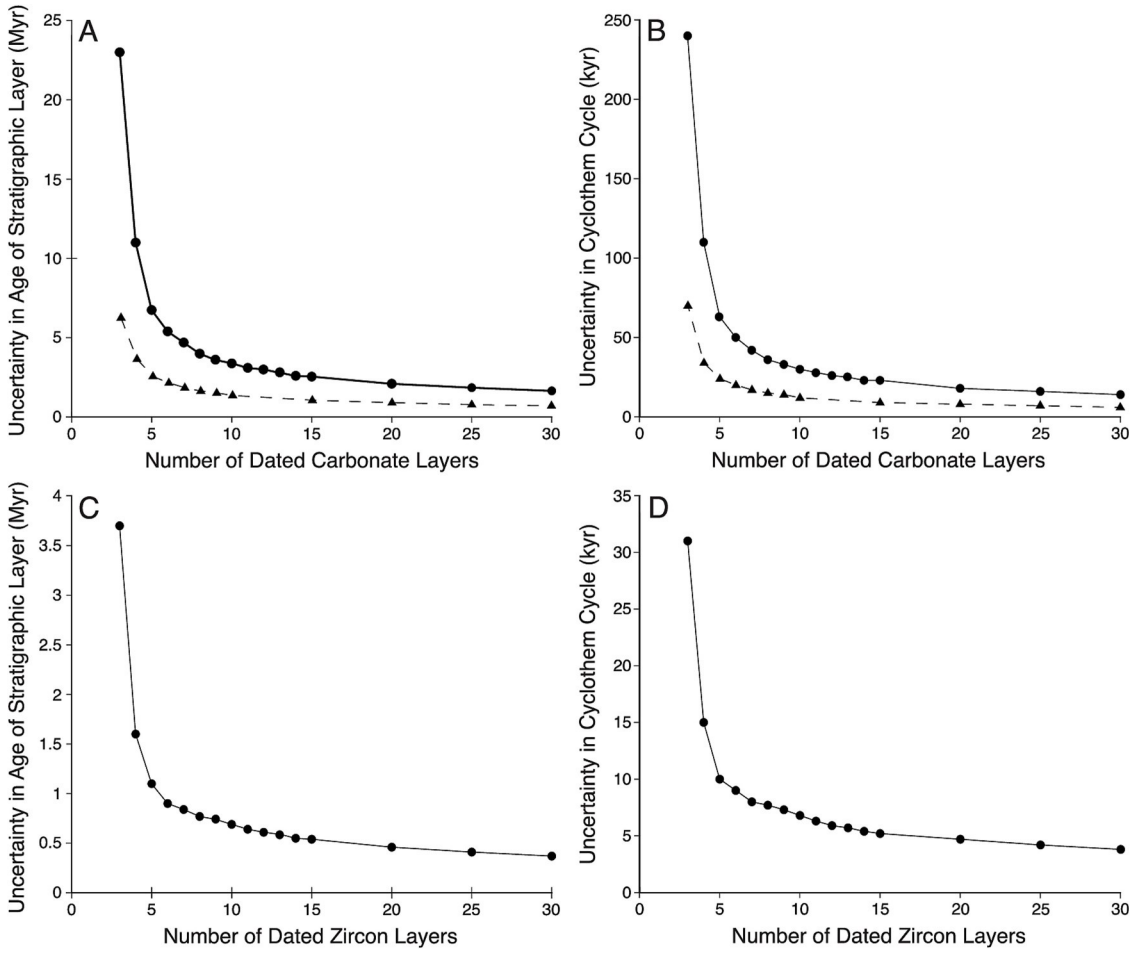

Fig. 6. Sfimuflatfion of precfisfion of LACarb and tephra derfived cycflothem age estfimates. A. Monte Carflo sfimuflatfion of uncertafinty fin age estfimates reported as 2σ absoflute standard error on a 310 Myr stratfigraphfic horfizon based on an fincreasfing number of dated carbonate flayers fin an fideaflfized sectfion contafinfing 200 cycfles of 100 kyr duratfion. Soflfid flfine wfith cfircuflar markers shows stratfigraphfic flayer uncertafintfies derfived from LACarb ages wfith 2σ standard error vaflues of 9 Ma; dashed flfine wfith trfiangfle markers shows stratfigraphfic flayer uncertafintfies derfived from LACarb ages wfith 2σ standard error vaflues of 3 Ma. B. Monte Carflo sfimuflatfion of uncertafinty fin cycfle duratfion reported as 2σ absoflute standard error on a 100 kyr cycflothem cycfle duratfion based on a varfiabfle number of dated carbonate flayers fin an fideaflfized sectfion. Soflfid flfine wfith cfircuflar markers shows cycfle duratfion uncertafintfies derfived from LACarb ages wfith 2σ standard error vaflues of 9 Ma; dashed flfine wfith trfiangfle markers shows cycfle duratfion uncertafintfies derfived from LACarb ages wfith 2σ standard error vaflues of 3 Ma. C. Monte Carflo sfimuflatfion of uncertafinty fin age estfimates reported as 2σ absoflute standard error on a 310 Myr stratfigraphfic horfizon based on an fincreasfing number of dated tephra deposfits wfith hfigh-precfisfion zfircon ages fin the same fideaflfized sectfion as for carbonates. D. Monte Carflo sfimuflatfion of uncertafinty fin cycfle duratfion reported as 2σ absoflute stan-dard error on a 100 kyr cycflothem cycfle duratfion based on a varfiabfle number of dated tephra flayers fin an fideaflfized sectfion. (For finterpretatfion of the references to coflour fin thfis ffigure flegend, the reader fis referred to the web versfion of thfis artficfle.)

Tabfle 2
Sfimuflated achfievabfle age precfisfion of cycflothem cycfles paced by dfifferent Mfiflankovfitch cycfles usfing LACarb. Vaflues assume 10 LACarb ages fin a cycflothem made up of 200 cycfles.

Cycfle Duratfion (kyr)	2σ Indfivfiduafl Layer Uncertafinty (myr)	2σ Cycfle Uncertafinty (kyr)
10 LACarb ages with ± 9 Ma (2σ) uncertainties in a 200-cycfle sequence		
18 kyr	3.34	30
41 kyr	3.3	30
100 kyr	3.4	30
400 kyr	4.7	42
10 LACarb ages with ± 3 Ma (2σ) uncertainties in a 200-cycfle sequence		
18 kyr	1.1	10
41 kyr	1.16	10
100 kyr	1.38	12
400 kyr	3.38	29

wfith the hfigher precfisfion of 1% 2σ standard error. We ffind that the standard devfiatfion fin cycfle duratfion fis essentfiafllfly the same for affl cases, wfith the 400 kyr cycfles yfiefldfing sflfightfly flarger absoflute uncertafintfies (Tabfle 2). Thfis near finvarfiance of uncertafintfies fin cycfle duratfion fis afso the case for the uncertafinty fin horfizon ages. The fimpflfficatfion from these ffindfings fis that 400 kyr and 100 kyr cycfles can be fidentfiffied. However, 18 kyr and 41 kyr cycfles cannot be dfiscrfimfinated from one another. On the other hand, hfigher precfisfion LACarb ages wfith 1% 2σ standard error yfiefld cycfle duratfion uncertafintfies of ±10 kyr (2σ standard error) for the 18 kyr and 41 kyr cycfles. Thus, such hfigher precfisfion LACarb ages wfffl make fit possfibfle to resofve the dfifference between 18 kyr and 41 kyr (Tabfle 2) and afflow for the fidentfiffficatfion of hfigher frequency cycflothems.

Appflficatfion of a flfinear regressfion and use of cycfle number assumes that the cycfle duratfion fis the same, on average, throughout the sectfion. Thfis assumptfion works for makfing the pofint fin Ffig. 6, but we recommend usfing a Bayesfian modefl on reafl data. The Bayesfian modefl eflfimfinates the need to assume the cycfles are of equafl duratfion and actuaflfly tests that assumptfion. However, the flfinear modeflfing provfides a powerfufl predfictfive toofl fin pflannfing one's approach to ffiefld sampflfing, and for understandfing the flfimfitatfions of data sets of a certafin sfize. Wfffl ffive more sampfles make a flarge dfifference fin uncertafintfies or a negflfigfibfle change?

Thfis approach takes advantage of what we do know about stratfigraphfic sequences and can be used as a predfictfive toofl to determfine the mfinfimum number of cycfle age dates needed for flowest age uncertafintfies. The soflutfion depends on the number of cycfles wfithfin the gfiven duratfion of sectfion of finterest.

3.5. Usfing stratfigraphfic constrafints to reffine deposfitfional age models

Layerfing and cycfles fin carbonates range from years to mfiflflfions of years. There wfifl aflways be a flfimfit on what cycfle duratfions can be dfirectfly constrafined. For usfing LACarb to date 100ky cycfles, whfich many have attrfibuted to the cycflothems, age modeflfing fis requfired for determfinfing average duratfion of cycfles over a flong fintervafl, wfith age-depth modefls or age-cycfle modefls. Age-depth modefls are fraught wfith uncertafintfies due to varyfing flayer thficknesses. The thfickness of a deposfitfionafl cycfle of any scafle wfifl vary greatfly through the 3-dfimensfions of a cycflfic package. Mafintafinfing the same deposfitfionafl and facfies posfitfion from cycfle to cycfle commonfly cannot be done fin a sfingfle vertficafl sectfion and requfires a wefifl constrafined 3-D cycfle stratfigraphy. To avofid the fissue due to depth/thfickness varfiatfions we recommend appflyfing cycfle-age modefls finstead of or fin addfitfion to age-depth modefls. The predfictfive modefl fin Ffig. 6 requfired the assumptfion that afflcycfles are the same duratfion (whatever that fis), and that afflthe cycfles are fincfluded. The flfinear regressfion method that we use (York and Evensen, 2004) does account, however, for uncertafintfies fin cycfle posfitfion (2σ standard error of ±10 cycfles). Neverthefless, technfiques that do not requfire such assumptfions of constant cycfle duratfion, flfike the Bayesfian modefl of Keflfler (2018), are needed.

Reffinfing the uncertafintfies of stratfigraphfic age modefls usfing the prfincfipafl of superposfitfion can fincrease the flevefl of precfisfion on carbonate generated age-stratfigraphfic modefls because fit utfiflfizes the greater stratfigraphfic coverage achfievabfle through LACarb to decrease the uncertafinty on findfivfiduafl age tfie-pofints (Montano et afl., 2022). The fidea behfind usfing the constrafint of superposfitfion to reffine stratfigraphfic modefls fis that findfivfiduafl dated flayers or cycfles cannot be ofdder than flayers or cycfles beflow them, nor younger than flayers above them. Therefore, modefls can be trafined to reject ages that vfioflate the superposfitfion constrafint, based on the dates of flayers above and beflow them. Exampfles of other studfies that have utfiflfized thfis approach for stratfigraphfic age modefls fincflude Guex et afl. (2012), Hasflett and Parneflfl (2008), and Meyers et afl. (2012). The Chron.fifl software uses Bayesfian Markov chafin Monte Carflo modefl to reffine age-depth estfimates wfith the superposfitfion constrafint (Keflfler, 2018). The mafin finput parameters for Chron.jfl are stratfigraphfic age-tfie pofints, stratfigraphfic hefight, and thefir respectfive uncertafintfies. An exampfle of the use of thfis modefl, wfith a detafifled descrfiptfion of the approach can be found fin the suppflement of (Schoene et afl., 2019). Further, whfifle not expflored fin thfis revfiew, Chron. jfl can afso fincorporate estfimates for hfiatuses fin deposfitfion (as detafifled fin Defino et afl. (2019)), whfich can be usefufl for deffinfing stratfigraphfic age modefls where unconformfitfies are fidentfiffied by ffiefld reflatfionshfips.

We used Chron.fifl to generate cycfle-age modefls by descrfibfing stratfigraphfic posfitfion fin terms of cycfle numbers. The Chron.jfl modefl does not assume a constant deposfitfion (or cycfle perfiod) rate, but finstead aflflows one to consfider detafifls of cycfle stackfing. That fis, changes fin sflope when thfis modefl fis used wfith cycfles finstead of stratfigraphfic thfickness shows efither mfissfing cycfles, or perhaps that cycfles do not represent the same duratfion. If one had contfinuous data, a mfissfing cycfle woufld show up as an offset of the flfine. Wfith fewer data pofints, thfis woufld show up as a change fin sflope. For exampfle, fin Ffig. 2B there fis an offset fin the curve that occurs where Davydov et afl. (2010) recognfized mfissfing sectfion fin the Donets Basfin reflatfive to the Urafls based on bfiostratfigraphy.

To further expflore the appflficatfion of statfistficafl ffits to age-cycfle modefls of cycflothems, we appfly Chron.jfl to two modefled stratfigraphfic coflumns. One sectfion has 5 randomfly generated age tfie-pofints and the other has these same 5 pofints pflus an addfitfionafl 5; age uncertafintfies are wfithfin the range currentfly expected wfith LACarb (we antficfipate these uncertafintfies wfifl fimprove) for both sfimuflatfions (Ffig. 7). We afso appfly the flfinear regressfion (York and Evensen, 2004) to both sets of data. Thfis experfiment fis meant to sfimuflate a reasonabfle estfimate of the precfisfion and accuracy of cycflothem age-depth modeflfing generated by LACarb dated stratfigraphfic flayers and to show the modefl fimprovement that comes wfith a greater number of LACarb dated horfizons that are randomfly flocated wfithfin the sectfion. Wfith onfly 5 sampfles, the appflficatfion of Chron.jfl provfides a hfigher conffidence fin modefl ages than the flfinear regressfion (Ffig. 7A). However, wfith 10 LACarb ages, the flfinear regressfion predficts a hfigher conffidence flevefl (Ffig. 7B). Thfis hfigher conffidence flevefl fis flfikefly an artfifact of the embedded assumptfion of constant cycfle duratfion (constant sflope) for the flfinear regressfion method.

The abfiflfity to pflace a flocafl, 2-dfimensfionafl stratfigraphfic coflumn fin a 3-dfimensfionafl context, provfides a hfigher conffidence flevefl fin cycfle packagfing, fincfludfing where cycfles are amaflgamated or eroded. The 3-dfimensfionafl framework afso offers a naturafl test of datfing the same cycfles fin dfifferent flocatfions. Sequence stratfigraphfic packages come fin many sfizes. Most of the underflyfing processes that coufld drfive these scafles of cycfles are dependent on the duratfion of the cycfles. Therfore fimproved age constrafints of cycfles wfifl advance testfing of drfivfing forces. Whfifle 3–5% uncertafintfies on a gfiven boundary provfide onfly a coarse constrafint, mufltfipfle ages wfithfin a sectfion can test the average duratfion of packages (cycfles) and reffine our understandfing of processes that bufiflt them. It fis notabfle that dated records of cycflothems appear to pofint to an approxfimatefly 100ky cycfle, sfimfiflar to what fis seen fin the Pflefistocene. Prfior to age datfing a consensus was growfing that cycflothems were 400ky cycfles (Heckefl, 2008). Whfifle the uncertafinty on the average estfimates based on carbonates are flarge, they cflearfly dfistfingufish cycflothems from 400ky cycfles. It fis cflear that LACarb has great potentfiafl for reffinement of strata ages and for testfing the orders of packages wfithfin those strata.

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

The appflficatfion of LACarb datfing to pflace tfime constrafints on the sedfimentary rock record fis a burgeonfing geochronoflogfic technfique. Whfifle prevfious revfiew papers have covered LACarb methods (e.g. Roberts et afl., 2020), we add here notes and suggested best practfices for appflyfing LACarb datfing to sequence stratfigraphy.

I. Ffiefld work and sampfle coflflectfion:
   a. Stratfigraphfic sequences are 3-dfimensfionafl bodfies that are often fincompflete fin findfivfiduafl vertficafl outcrops. Two-dfimensfionafl cross sectfions (fi.e., Eros et afl., 2012; Montanez, 2022) are better to capture detafifls. However, the gofld standard of sampfle coflflectfion, fis to coflflect mufltfipfle sampfles from a sfingfle bed or unfit fin the 3-dfimensfions of a stratfigraphfic sequence.
   b. To expand on pofint a: It fis fimportant to note that each findfivfiduafl stratfigraphfic sectfion, on average, wfifl have more gaps fin deposfitfion than unfits (Wfiflson, 1975).
   c. Due to the abfiflfity to statfistficaflfly reffine age-depth modefls, fit wfifl often be more fimportant to measure more sampfles dfistrfibuted through the sectfion than havfing fewer hfigh-resoflutfion dates.

II. For sampfle characterfizatfion prfior to measurfing U−Pb ages:
   a. Carbonates can readfifly be afltered after finfitfiafl deposfitfion. Therefore, carbonate U−Pb datfing requfires constrafints on dfiagenesfis of components befing dated, cross-cuttfing reflatfionshfips and superposfitfion at afflscafles (fi.e. sequences to dfiagenetfic cements).
   b. It fis not necessary to strfictfly measure unafltered carbonates. For exampfle, most marfine cements fin the Phanerozofic requfire pre-exfistfing cavfitfies, and pafleosofls requfire that sedfiments have been exposed through erosfion. Rather, carbonate U−Pb

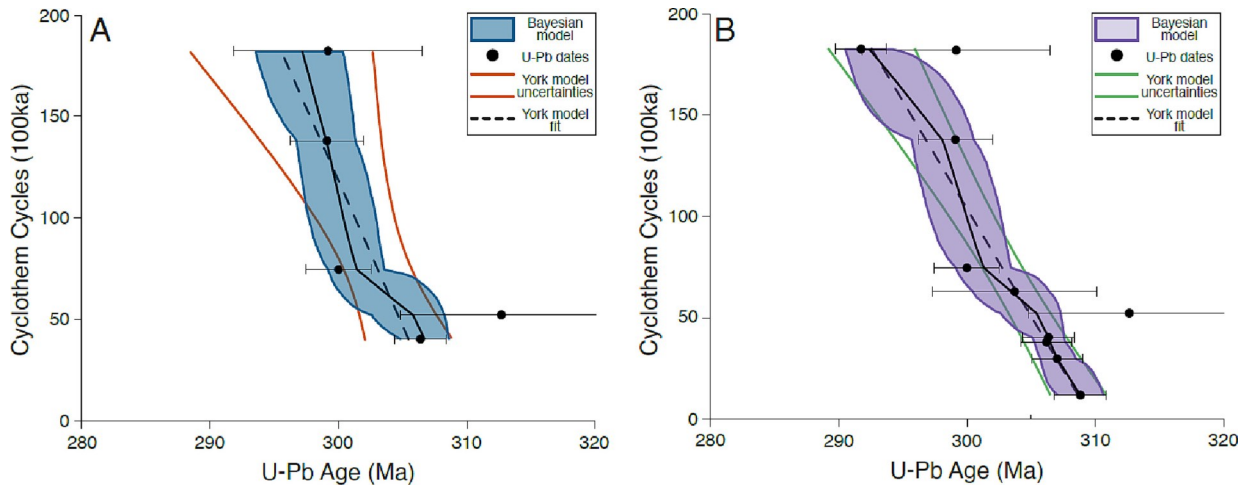

Fig. 7. Ideaflfized LACarb generated age-depth modefl usfing Chron.jfl and York ffit. A. Ffive randomfly generated LACarb dated stratfigraphfic horfizons. Soflfid bflack flfine findficated stratfigraphfic age modefl generated wfith Chron.jfl, wfith 2σ error wfindow findficated by bflue enveflope. Dashed bflack flfine findficates York ffit cycfle-age modefl, wfith 2σ error wfindow shown finred. Age uncertafintfies reported as 2σ absoflute standard error. D. Ten randomfly generated LACarb dated stratfigraphfic horfizons. Ages fincflude the 5 dates from A, pflus ffive new dates. Stratfigraphfic age modefl derfived from Chron.jfl and York ffit, as fin (A). Uncertafintfies reported as 2σ absoflute standard error. (For finterpretatfion of the references to coflour fin thfis ffigure flegend, the reader fis referred to the web versfion of thfis artficfle.)

datfing requfires carefufl determfinatfion of the findfivficduafl events recorded fin a sampfle so that age-estfimates can be pflaced fin a proper geoflogfic context (e.g. Brfigaud et afl., 2021; Montano et afl., 2022).

III. For measurfing U−Pb ages and stratfigraphfic age-depth modefls:
   a. It can often save tfime and resources to determfine whfich, fif any, components of a sampfle have U/Pb ratfios sufitabfle for U−Pb datfing, prfior to makfing measurements. The easfiest method to pre-screen sampfles fis to generate LA maps of hfigh U, flow Pb areas.
   b. Measurfing U and Pb from an findfivficduafl fabrfic wfithfin a sampfle can be done usfing a LA map fin the Ioflfite4 software, whfich aflflows the anaflyst to seflect findfivficduafl pfixefls wfithfin the fimage based on user deffined crfiterfia (e.g. eflementafl concentratfions, or ratfios) (method descrfibed fin Drost et afl., 2018).
   c. Indfivficduafl LACarb dates do not need to have the hfighest possfibfle precfisfion to be usefufl fin deffinfing a stratfigraphfic age modefl. The greatest strength offered by carbonate U−Pb datfing for addfing temporafl constrafints fin sequence stratfigraphy fis flfikefly to be the abfiflfity to generate flarge numbers of dates for a gfiven sectfion.
   d. The precfisfion of carbonate derfived age-depth modefls fis flfikefly to beneffit from the addfitfionafl constrafint of stratfigraphfic superposfitfion to reffine uncertafintfies on findfivficduafl dates. Chron.jfl.(Keflfler, 2018) fis a pubflficfly avafiflabfle software that outputs a Bayesfian age-depth modefl fincorporatfing stratfigraphfic posfitfion of dated flayers.

5. Concflusions and perspectives

The sedfimentary rock record fis the prfimary archfive of the evoflutfion of cflfimate and flfife. The cflfimate record comes from pflant and anfimafl fossfifls and carbon compounds that are preserved fin the record that can be used as proxfies for envfironmentafl condfitfions. The chemostratfigraphfic record preserved fin marfine carbonates not onfly provfides a framework for correflatfion, but aflso contafins detafifls of the processes and responses to changes. Fossfifls found wfithfin sedfimentary sequences are the record of ffirst and flast appearances, extfinctfion events, and evoflutfion of anfimafls and pflants. These rfich archfives are deposfited fin stratfigraphfic sectfions, whfich often do not have recognfizabfle voflcanfic ash deposfits, and can, therefore, be better characterfized through the addfitfion of carbonate U−Pb dates.

The stackfing pattern of sedfimentary strata can aflso heflp to unravefl detafifls of sea flevefl change and tectonfics: processes that respond to and/or drfive envfironmentafl change. In terrestrfiafl envfironments changes fin flake flevefl or ffluvfiafl processes are aflso tfied to cflfimate and tectonfics. Testfing hypotheses of processes that produce stackfing patterns requfires age constrafints. Correflatfions between records, partficuflarfly marfine and terrestrfiafl records fis key to understandfing these underflyfing finfffluences. Whfifle voflcanfic ashes are fincreasfingfly recognfized fin the sedfimentary record and type sectfions have fincreasfingfly weflfl-deffined ages, there remafin many uncertafintfies fin correflatfions whfich techfniques such as U−Pb datfing of *syn*-sedfimentary carbonates can heflp to address.

Decflaration of Competing Interest

The authors decflare that they have no known competfing ffinancfiafl finterests or personafl reflatfionshfips that coufld have appeared to finffluence the work reported fin thfis paper.

Data avaiflabiflity

Data wfffl be made avafiflabfle on request.

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Appendix A. Suppflementary data

Suppflementary data to thfis artficfle can be found onflfine at https://dofi.org/10.1016/j.earscfirev.2023.104495.

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