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Interactive comment on "LA-ICPMS U-Pb geochronology of detrital zircon grains from the Coconino, Moenkopi, and Chinle Formations in the Petrified Forest National Park (Arizona)" *by* George Gehrels et al.

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==> Review comments inserted below (Responses regarding stratigraphy are mainly from William Parker, responses regarding geochronology are from George Gehrels)

JR: This manuscript is part of a series of contributions from the Colorado Plateau Coring Project (CPCP), including Olsen et al. (2018), Kent et al. (2018), Kent et al. (2019)

and Rasmussen et al. (in review), which aim to construct a chronostratigraphic model for the subsurface Chinle Fm. strata at the Petrified Forest National Park (PEFO), for which a high-resolution chronostratigraphic framework has already been established based on integrated outcrop stratigraphic and CA-ID-TIMS geochronologic works of Ramezani et al. (2011: RA'11) and Atchley et al. (2013: AT'13). Here I review the data and conclusions of the manuscript under two main categories of Stratigraphy and U-Pb geochronology.

Stratigraphy ...

The Chinle Fm. is a package of alluvial (flood-) plain and fluvial channel deposits characterizes by vertically repetitive and laterally discontinuous sedimentary facies. Within the geographic boundaries of PEFO, correlation of the Chinle Fm. outcrops has been aided by a number of known 'key beds' such as the Newspaper Rock bed, Rainbow Forest/Jasper Forest beds, Flattop Sandstone beds, Painted Desert Sandstone beds, Black Forest bed, etc. Whereas the CPCP contributions have explicitly stated or implicitly indicated a high degree of confidence in their core-outcrop correlations, the underlying evidence for such confidence have not been laid out.

==> This is misleading. Other than the Black Forest bed and the persistent red 'silcrete' the team has not tried to identify bed-level stratigraphy in the core. The member designations match lithologically and are roughly consistent with outcrop correlations.

JR: Since the coring began near the surface outcrops of the Black Forest bed, it is safe to assume that this marker horizon was reliably identified in the core. But there has been no mention of any of the key beds being intercepted in the core. The manuscripts describes from the core a reddish siliceous horizon (Lines 140-142) of presumed biostratigraphic significance (in the outcrop). Martz and Parker (2010) report at least 3 such 'silcrete' horizons from outcrops of the Sonsela Mbr (labeled red, orange and black silcrete beds), so it is not clear precisely which one was intercepted in the core

==> We have backed off from having a specific silcrete horizon identified in the core.

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Lines 56-59: These complications challenge attempts to establish a well-defined chronostratigraphic age model for the Chinle Formation. ==> Have removed "and to evaluate possible connections among fundamental Late Triassic biotic and climatic changes and a red siliceous horizon encountered in the CPCP core."

Lines 804-807: . . . The occurrence of very different <240 Ma ages, >240 Ma ages, and U/Th values in samples 196-3 and 195-2 suggests that this unconformity most likely coincides with the boundary between lower and upper Sonsela Member strata. ==> Have removed "and perhaps with the red siliceous horizon recognized in the CPCP core."

Lines 897-899: . . . Significant changes in <240 Ma ages, >240 Ma ages, and U-Th values suggest that this unconformity, if present, occurs between samples 196-3 and 195-2. ==> Have removed "and may coincide with the red siliceous horizon recognized in the CPCP core."

JR: To make the matter worse, the Moenkopi Fm., as well as the Mesa Redondo, Blue Mesa and parts of the Sonsela Mbr are all predominated by ‘reddish mudstones and interbedded sandstones’ (Section 2). These units tend to weather differently in the outcrop due to compositional differences (e.g., volcanic ash content) and produce distinct landscapes throughout the Colorado Plateau. But in the fresh core and without the aid of marker beds, it is not clear at all how their mutual boundaries can be recognized.

==> There are differences, lower Chinle sediments are bentonitic and have a very high mica content (Martz and Parker, 2010). It is also important to point out that the member-level and bed-level units throughout the Chinle at PEFO were described from fresh, unweathered rock and that determining them in outcrop AND the core with lithological characteristics can and is quite easy to do. The purpose of this paper is not to rehash definitions of formal and informal lithostratigrapic units, but we provide all of the necessary citations to pull them from the literature.

JR: The manuscript suggests that the Shinarump Member (conglomerate) of the Chinle

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Formation is a lateral correlative of the finer-grained strata of the (entire) Mesa Redondo Member, implying that the presence of Mesa Redondo lithologies explains the absence of Shinarump conglomerate from the core. This view is not supported by previous detailed stratigraphic studies, the most relevant of which is Stewart et al. (1972). These workers described the stratigraphy of the basal Chine Fm. near St. John's, AZ (50 km SE of PEFO) as consisting of 5.1m of mottled strata, 10.2m of Shinarump Member and 25.8m of Mesa Redondo Member, clearly distinguishing between these units stratigraphically. In fact the basal Mesa Redondo Mbr in the Hunt Valley area (23 km SE of PEFO) consists of a >10m thick conglomerate that could conceivably correlate with Shinarump (RA'11), but the overlying 15m of the Mesa Redondo strata clearly overlie – and are thus younger than – the conglomerate, as demonstrated by the outcrop U-Pb geochronology of RA'11 and AT'13. Therefore, the total absence of the Shinarump/Mesa Redondo conglomerate (and other key horizons) from the core is alarming and puts into serious question the accuracy of stratigraphic orientation of the core.

==> It has been very difficult to use sections in these older studies for current outcrop work, in particular at the base of the Chinle. It is not clear at all what strata Stewart et al., 1972 considered to be the Mesa Redondo. Through our detailed work we have never seen superimposed Shinarump and Mesa Redondo and we have interpreted this to mean that they represent lateral facies changes from channel to overbank. One key piece of support is that the tops of these units are distinctly pedogenically modified and have a very strong "4-colored" mottling. This always occurs below the contact with the unambiguous overlying Blue Mesa Member. This is different from the "Mottled Strata" that is exposed primarily to the north in southern Utah and represents pedogenesis of the top of the Moenkopi Formation. Thus, the Stewart et al., 1972 section is most likely Moenkopi, Shinarump (rather than the Mesa Redondo), and then lower Blue Mesa.

JR: Considering the above issues and based on the observation that the subsurface and outcrop geochronologies appear fairly consistent near the top of the core and begin to deviate at depth, reaching a maximum bias of >3 myr near the base of the Chinle Fm., the first-order suspicion should be that the core stratigraphy may not not accurate.

==> The Moenkopi is unambiguous. Also in the two cores, one has conglomerate at the base of the Chinle, and the other has redbed mudrocks in the same stratigraphic position. There accordingly is little uncertainty about the member-level correlations between core and outcrop [see Figure 4 of Kent et al. (2019]. The reviewer is encouraged to provide an alternate interpretation of the units in the core.

JR: Unless clearly identifiable bed or beds are intercepted, this inaccuracy is expected to increase with depth, consistent with the observation. To produce a meaningful age model, the manuscript needs to quantitatively assess the stratigraphic uncertainty in the core as a function of depth.

==> This manuscript does not attempt to establish an age model.

JR: U-Pb Geochronology ...

Notwithstanding that the U-Pb geochronologic data of this study provide invaluable insights into the sedimentary provenance of the Triassic formations of the Colorado Plateau, their depositional age interpretations have been highly problematic. Although the manuscript touches upon the issue of Pb loss in the analyzed zircons, neither its severity nor its impact on depositional age interpretations have not been properly addressed.

It is claimed that the U concentrations (ppm) of the analyzed zircon can be used screen out analyses compromised by Pb loss. In particular, it is suggested that the U concentration of the youngest zircon compared to the average U concentration of the youngest cluster of analyses can determine whether or not the youngest date is an outlier. This relationship has never been proven and the data of this study actually indicate the opposite. Of the 3 samples from which the youngest analyzed zircon has come out Jurassic in age (92-2, 196-3 and 297-2), two have shown to have a significantly lower

U content than the average of the youngest cluster (150 and 165 ppm, compared to 240 and 340 ppm, respectively), and the U content of the third one (502 ppm) overlaps with that of the youngest cluster (439 ppm) within the inaccuracy of U measurements (20%, footnote 10 of Table DR3).

==> Reviewer is incorrect – nowhere in the paper do we claim that Uconc can be used to screen out analyses because they are compromised by Pb loss. We use the long-established observation that Pb loss tends to correlate with Uconc to test for evidence that analyses in the youngest cluster may have lost Pb. If yes, we note that the max depo age calculated from the youngest cluster may be too young due to Pb loss. If no, there is no evidence to support this conclusion. Nowhere do we do any filtering based on Uconc! In more detail, as described on lines 269-280 of the manuscript and reported in DR Table 6, we test for correlations between age and Uconc in two ways: 1. Uconc of the youngest analysis is compared with Uconc of the youngest cluster. If the youngest age has higher-than-average Uconc, there is evidence that the youngest analysis, and perhaps analyses in the youngest cluster, may have experienced Pb loss. 2. Uconc is plotted against age for all analyses in the youngest cluster. If younger grains tend to have higher Uconc, there is evidence that some or perhaps all ages in the youngest cluster have experienced Pb loss.

JR: The fact is that at present, no a priori indicator of Pb loss exists. Once one or more analyses from a samples are empirically shown to be compromised by Pb loss, the remainder of its analyses are likely to be compromised to varying degrees as well, and the extent of Pb loss cannot be in any meaningful way modelled by looking at U concentration or any other compositional parameter. The large inaccuracy of U and Th measurements by LA-ICPMS (20%) makes these parameters even less useful.

==> This is exactly what our procedures are designed to evaluate – whether there is empirical evidence that analyses in the youngest cluster have been compromised by Pb loss. The results are not used to do any modelling (or filtering), they just provide a means of identifying samples for which there is evidence that Pb loss is an issue. With regard to the uncertainty of Uconc measurements, most of this uncertainty comes from session-to-session variations in Uconc of the standard grains analyzed (e.g., FC-1). If a session has hotter-than-average FC-1 grains, then Uconc of all unknowns from that session will be underestimated. But the relative Uconc values within a session, which is what we use to look for correlations between Uconc and age, will not be impacted by this systematic uncertainty. It's unlikely that the much smaller internal uncertainty of the measured Uconc values has resulted in misleading evidence for/against Pb loss.

JR: Most importantly, if the chemically abraded ID-TIMS analyses show unequivocal evidence of persistent Pb loss in at least some of the analyses, it would be only logical to conclude that the microbeam analyses of the same zircons will be compromised (even to a larger degree) by Pb loss, as well. There are several strong lines of evidence that suggest this can be the case here. First, initial outcrop CA-ID-TIMS zircon analyses from the upper Blue Mesa Mbr at PEFO (sample TPs) reported in RA'11 showed 2 outliers up to 3.3 myr younger than the cluster of 7 overlapping analyses used to calculate the weighted mean age of the sample. These analyses had been chemically abraded at 180 C for 12 hours. Once the leach intensity was increased to 210 C (for 12 hours), no such young outliers appeared in the remainder of the outcrop CA-IDTIMS U-Pb data reported in RA'11, AT'13 or Ramezani et al. (2014). Second, 2 out 4 CA-ID-TIMS zircon dates reported in Kent et al. (2018) from the CPCP core had visibly younger outliers (up to 4) excluded from age calculations due to insufficient treatment of Pb loss. Third, a comparison between the selected youngest LA-ICPMS zircon analyses and their corresponding CA-ID-TIMS dates in Rasmussen et al. (in review) illustrated in Appendix 2 points out to an even more pervasive Pb loss problem. Here the chemically abraded ID-TIMS analyses are systematically older than their untreated LA-ICPMS counterparts (Lines 585-586), but yet show a comparable data scatter, and a significant number of younger analyses have evidently been excluded in order to reach "preferred" CA-TIMS ages. For other examples of microbeam U-Pb geochronology leading to anomalously young age models due to Pb loss, the authors are referred to Wu et al. (2016) and Schmitz et al. (2019).

==> This manuscript goes to great length to document that Pb loss is a significant factor for many of the grains analyzed. We show this internally with the Uconc-age tests described above. We also document this by comparison of our ages with the CA-TIMS data from the same grains (Appendix 2). Indeed, Pb loss is an important factor for many of our analyses! But the assertion that LA-ICPMS max depo ages are younger than the CA-TIMS ages of Ramezani et al. (2011) and Atchley et al. (2013) due to Pb loss is not supported by the fact that most of the reported LA-ICPMS MDA's are older (not younger) than the equivalent MDA's reported by R+2011 and A+ 2013!! This is best shown for samples in the upper Chinle (Petrified Forest and upper Sonsela members of Fig 13), where there is little uncertainty about stratigraphic correlation, and there is excellent agreement (within 1 m.y.) between the CA-TIMS data of R+2011 and A+2013, the CA-TIMS data of Rasmussen et al. (2020), and the magnetostrat age model of Kent et al. (2019). For the Black Forest Bed of the Petrified Forest Member, our ages of ∼209.8 and ∼209.6 Ma are indistinguishable from the CA-TIMS ages of ∼209.9 Ma (R+2011) and ∼210.2 Ma (Rasmussen et al., 2020). For strata of the upper Sonsela Member, the LA-ICPMS ages are consistently older than the available CA-TIMS ages: Sample 158 yields a LA-ICPMS age of ∼213.8 Ma, whereas the corresponding CA-TIMS age is ∼213.5 Ma. Samples 188, 182, 172, and 169 yield LA-ICPMS ages ranging from ∼215.1 to ∼216.6 Ma, whereas the four CA-TIMS ages from equivalent strata range from ∼231.1 to ∼214.0 Ma. LA-ICPMS ages are also older than most CA-TIMS ages from lower Chinle strata, although this comparison has greater uncertainty because of issues of core-outcrop correlation (described above). For strata of the lower Sonsela Member, samples 210 and 201 yield LA-ICPMS ages of ∼220.9 and ∼220.6 Ma, significantly older than the R+2011 age of ∼218.0 Ma, and samples 227 and 215 yield LA-ICPMS ages of ∼220.6 and ∼220.5 Ma, significantly older than the R+2011 age of ∼219.3 Ma. For the lowermost Sonsela Member and the uppermost Blue Mesa Member (samples 261 and 243) LA-ICPMS ages are ∼220.7 and ∼220.3 Ma (respectively), again older than the R+2011 age of ∼220.1 Ma from the uppermost Blue Mesa. At issue are the three CA-TIMS ages reported by R+2011 and A+2013

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from underlying strata of the Blue Mesa and Mesa Redondo members, given that LA-ICPMS ages from equivalent(?) strata (samples 305, 297, 287, and 261) are 2-3 m.y. younger. Given that all LA-ICPMS ages from overlying strata are older than or indistinguishable from corresponding CA-TIMS ages (described above), presumably these are the LA-ICPMS ages that the reviewer interprets to have been compromised by Pb loss. . .... As described in the manuscript, we interpret three of the four LA-ICPMS ages (for samples 305, 297, 287) to be reliable given that they overlap with CA-TIMS ages from the same grains (Rasmussen et al., 2020) and the magnetostrat age model (Kent et al., 2019). Sample 261 is interpreted to be older than the depositional age, but indistinguishable from samples 297 and 287, due to recycling of grains from underlying strata. Given these relations, and the evidence presented above that our LA-ICPMS MDA's are not compromised by Pb loss, we offer the possibility that the three ages reported by R+2011 and A+2013 from the Mesa Redondo and Blue Mesa members are too old due to the presence of older recycled zircons. An independent test of the reviewer's interpretation (that the lower four LA-ICPMS ages are too young due to Pb loss) is provided by a comparison of the suspect LA-ICPMS ages with ages from overlying strata. As the reviewer notes below, a powerful test of the reliability of max depo ages is whether they follow stratigraphic order. Within the four suspect LA-ICPMS ages, the Mesa Redondo sample yields an age of 223.3 Ma, which is significantly older than ages from overlying Blue Mesa strata (220.2-220.6 Ma). In turn, the Blue Mesa ages of 220.6, 220.2, and 220.7 Ma are indistinguishable from overlying lower Sonsela ages of 220.6, 220.9, 220.5, 220.6, 220.3 Ma (Fig. 13; DR Table 6). This test accordingly does not support the hypothesis that the four LA-ICPMS ages are compromised by Pb loss. In contrast, we conclude that the surprising reproducibility of all eight LA-ICPMS ages between 220.2 and 220.9 Ma strongly supports our interpretation that similar ages of zircons are present in all samples due to prolonged recycling of detrital zircons!

JR: To summarize, the validity of depositional ages derived from U-Pb zircon analyses of tuffs (and tuffaceous sediments) in a fluvial depositional system such as the Chinle Fm., as outlined by RA'11, depends on a) the ability to produce accurate and

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statistically meaningful weighted mean 206Pb/238U dates from the youngest clusters of analyses without involvement of young outliers, b) achieving the desirable degree of analytical precision to produce mutually distinctive maximum depositional ages from closely spaced tuff beds, and c) the extent to which these maximum depositional ages follow the stratigraphic order. A review of the LA-ICPMS (and CA-ID-TIMS) zircon dates presented in this manuscript (Table DR3, Fig. 13 and Appendix2) demonstrates that the data in general do not meet the above criteria for a valid depositional age constraint. The only exception perhaps is a brief stratigraphic interval between the so-called lower and upper Sonsela Member (encompassing samples 201, 196 and 195) where the criteria b and c seem to have been met. Interestingly, this is the same interval where RA'11 originally identified a hiatus or a series hiatuses in the Sonsela Member based on outcrop U-Pb zircon geochronology and calculated average sediment accumulation rates pointing to a condensed section.

==> We agree with the above assessment – nowhere does the manuscript claim that the LA-ICPMS ages provide reliable max depo ages. Rather, the main conclusion of the paper is that the LA-ICPMS ages are in most cases older than age models derived from magnetostratigraphy (Kent et al., 2019) and from CA-TIMS analyses (R+2011, A+2013; Rasmussen et al., 2020) due to recycling of detrital zircons from older strata. We did neglect to mention that R+2011 discussed the possibility of a hiatus or hiatuses near the middle of the Sonsela Member. This has been added to the revised manuscript (in the response to Sharman's review) as follows:

***** ... Previous workers have suggested the existence of a hiatus or hiatuses (Ramezani et al., 2011) or an erosional event (Rasmussen et al., 2020) at approximately this stratigraphic level, as shown by the preferred age model of Rasmussen et al. (2020) on Figure 13. The occurrence of very different <240 Ma ages, >240 Ma ages, and U/Th values in samples 196-3 and 195-2 suggests that this shift in provenance, condensed section, or unconformity likely coincides with the proposed boundary between strata of the lower Sonsela Member and upper Sonsela Member. As discussed by Ramezani et al. (2011) and Rasmussen et al. (2019), the possibility of an unconformity or condensed section near this stratigraphic position has important implications for Chinle stratigraphy and fundamental Late Triassic biotic and climatic changes. It should be noted, however, that no stratigraphic evidence for such an unconformity was recognized in the CPCP core. . . . *****

JR: It is notable that the outcrop samples SS-28 (Mesa Redondo Member) and SBJ (lower Sonsela Member) dated as part of the RA'11 and AT'13 geochronologic study were a clay-rich (altered) tuff and a tuffaceous (paste-like) fine siltstone, respectively. The former was in fact the closest dated sample to a true ash-fall tuff both in terms of petrography and zircon age distribution (no detrital outliers), as described in detail in RA'11 and its supplemental materials. Therefore, the notion that the apparent geochronologic discrepancies between the present study and those of the RA'11/AT'13 in the lower Chinle could have to do with detrital zircon input is not supported by evidence.

==> As described in the manuscript, our interpretation is that the presence/absence of older detrital grains is controlled more by the depositional environment and provenance of a stratigraphic sequence than by the rock type sampled. This is suggested by the observation that adjacent samples from a stratigraphic sequence tend to have similar age distributions, even if they have very different grain size. For example, samples 116 and 104 yield indistinguishable age distributions, yet one is a sandstone and the other is a mudstone. We suggest that they both record near-depositional ages because this portion of the Petrified Forest Member consists of floodplain sediments that are dominated by air-fall zircons (in the >60 um size range that has been analyzed). Same with sample 210 (a siltstone) between 215 and 201 (both sandstones) – all three yield identical age distributions, but in this case the ages significantly predate deposition because this part of the Sonsela consists of sediments that accumulated in fluvial channels and are dominated by recycled grains. We accordingly offer the same interpretation for the SS-28 and SBJ – perhaps these fine-grained samples accumulated in a sedimentary system dominated by fluvial channels shed from the active Triassic arc, and accordingly are dominated by recycled detrital zircons.

JR: On a final note, the Heckert et al. (2009) abstract ID-TIMS date of 220.9 ± 0.6 Ma referred to in the manuscript as a “blue Mesa Mbr” age constraint (upside down triangle in Fig. 13) in support of their age model is from an isolated outcrop in New Mexico (not Arizona) with dubious cross-state lithostratigraphic correlations to PEFO (see Ramezani et al., 2014). Irmis et al. (2011) presented a significantly younger IDTIMS date of 218.1 ± 0.7 Ma from the exact same bed in New Mexico, which has not been mentioned here. Neither can be used to support the PEFO age model of this manuscript because of correlation uncertainties.

==> This age has been removed from the discussion and from Figure 13!

JR: A note about magnetostratigraphy ....

The subsurface magnetostratigraphic study of Kent et al. (2019) from PEFO has resulted in stratigraphic ages for the lower Sonsela, Blue Mesa, and Mesa Redondo members that are at odds with the outcrop U-Pb geochronology of RA’11 and At’13, as well as much of the lower Chinle subsurface geochronology presented in this manuscript. In particular, their magnetostratigraphic model does not recognize the mid-Sonsela interval of condensed stratigraphy (caused by depositional gap or gaps) identified by RA’11, resulting in an anomalously young, downhole age model. The main reason for this discrepancy appears to be that Kent et al. (2019) have chosen to correlate their Sonsela Mbr magnetostratigraphy to Chron E14 of the Newark-Hartford geomagnetic polarity time scale (216-213 Ma) irrespective of the independent radioisotopic age data from that interval. Their magnetostratigraphic interpretation assumes that the PEFO core record is continuous to the point that every single Newark-Hartford GPTS chron has been preserved in the core. Neither the lithologic characteristics of the Sonsela Mbr (incised fluvial channel deposits including massive conglomerates with extra-basinal clasts forming laterally continuous erosional surfaces: Martz and

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Parker, 2010)

==> This is not correct. Within the Sonsela Member the only beds with extrabasinal clasts are the Jasper Forest bed, and the Marthas Butte beds, and the only unit with massive conglomerates is the Jasper Forest bed. However, the JFB is strongly laterally variable and varies in thickness from 20-30 meters to less than a meter and also lithologically from conglomerate to sandy siltstone (Martz and Parker ‘10). In some places the unit is incised (thick channels) yet in others it is flat lying and conformable (overbank). Neither the sedimentology or the paleontology support the presence of a significant hiatus at the base (Parker and Martz ‘11).

JR: nor the bulk of U-Pb geochronology from the lower Chinle Formation support the magnetostratigraphic interpretation of Kent et al. (2019).

==> In response to the general statements concerning the validity of the magnetostratigraphic interpretations, we refer readers to the papers of Kent et al. (2018, 2019) and Rasmussen et al. (2020). These papers fully explore the assumptions inherent in the age models, and Rasmussen et al. (2020) discuss the presence/absence of Chron E14 in a comprehensive fashion.

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