Reply to Comments by Weixing Li

Thank you for the constructive comments and for reviewing our manuscript. We provide our responses to each major and minor comments below.

Reply to major comments:

>The claim that tracks in monazite retain a crystalline structure and lack amorphous features warrants significant caution. Conventional TEM alone is fundamentally incapable of resolving individual point defects or identifying latent track structures. To definitively distinguish true track-core features from the surrounding matrix, high-resolution TEM (HRTEM) combined with fast Fourier transform (FFT) or selected area electron diffraction (SAED) is strictly required. Because the authors did not perform HRTEM, their "crystalline structure" claim cannot be verified; without high-resolution lattice imaging, any observed lattice fringes may simply be an artifact of the electron beam projecting through the overlapping, intact crystalline matrix. This methodological limitation is further compounded by contradictions with prior work: Overstreet et al. (NIMB 2022) demonstrated the amorphization of ion tracks in Sm/Tb-monazite using conventional TEM, Raman spectroscopy, and XRD under GeV heavy-ion irradiation. Absolute assertions such as "no sign of amorphization" should be revised to reflect the resolution boundaries of the data (e.g., "no detectable complete amorphization"), and claims regarding "accumulated point defects" must be softened to acknowledge that conventional TEM cannot resolve such sub-nanometer features. Detailed technical limitations and alternative interpretations are provided in the minor comments below.

We thank the reviewer for highlighting the overstatement in our manuscript.

It should be emphasized that the TEM observations were performed along the same direction as the ion irradiation. Therefore, there should be no overlap between the ion track image and the surrounding matrix image.

In zircon, ion tracks are observed as amorphous circular features, and no lattice fringes are detectable within the tracks. This demonstrates that our experimental procedure is capable of reliably distinguishing whether an ion track is fully amorphous. For this reason, zircon was selected as a reference material, since it is well established that ion tracks in zircon are completely amorphous. Our observations are consistent with previous studies, demonstrating the reliability of our technique.

In contrast, the ion track images in monazite are clearly different from those in zircon. We believe this is a key point and that the reviewer will agree with its significance. The most important difference is that lattice fringes are detectable within the ion tracks in monazite, whereas no such lattice fringes are observed within the ion tracks in zircon.

Moreover, it should be noted also that the study by Overstreet et al. (NIMB, 2022) employed a 1.1 GeV Au ion beam. However, such a high-energy ion beam is not representative of the energies of fission fragments. The importance of this study lies in the adoption of a representative fission fragment energy of 80 MeV for Xe.

Nevertheless, we agree that the phrase “no sign of amorphization” was too strong and cannot be strictly substantiated by our conventional TEM observations alone. We also agree that conventional TEM cannot resolve sub-nanometer features related to point defects. Therefore, the conclusion will be modified in the revised version of the manuscript.

Accordingly, all instances of “non-amorphous tracks” will be replaced with “no detectable complete amorphization” as you suggested. And we will also refine the citation of the previous study by Overstreet et al. (2022) and will revise the discussion of accumulated point defects to reflect the resolution limits of conventional TEM observations.

>The manuscript would be significantly strengthened by explicitly comparing monazite with other key thermochronometer minerals, particularly apatite, which was omitted in this work, across track structure, formation and annealing kinetics, etching behavior, and closure temperatures. As the most widely used fission-track mineral (Gleadow et al., Rev. Mineral. Geochem. 2002), apatite exhibits continuous, highly porous tracks that anneal via distinct mechanisms (Li et al., EPSL 2011, EPSL 2012). This contrasts sharply with zircon’s fully amorphous, continuous tracks, and helps isolate the behavior of monazite’s own low-density, potentially discontinuous domains. Establishing this comparative framework is essential to explain why monazite exhibits an even lower closure temperature than apatite, and to properly contextualize monazite tracks within the known spectrum of latent radiation damage: fully amorphous in zircon, discontinuous, low-density tracks in TiO2 (Zhai et al., NIMB 2019), and continuous, highly porous in apatite. These fundamental structural variations govern long-term thermal stability and dictate how different minerals respond to chemical etching. Integrating these cross-mineral insights would elevate the study from an isolated, monazite-specific observation to a major, broadly applicable contribution to the field of thermochronology.

Originally, we intended to compare the nature of monazite FTs with that of zircon FTs, given their divergent track appearances (i.e., amorphous and non-amorphous), to simplify the discussion of the FT annealing mechanism. We will expand the discussion to include a systematic comparison of monazite with apatite, zircon and rutile (TiO_2), in line with your suggestions.

Reply to minor comments:

>Line 12: The authors appropriately selected 80 MeV Xe ions to simulate single fission fragments (70–100 MeV). However, the higher-energy ions (e.g., 300 MeV Kr) cited from the literature exceed typical fission energies and are unsuitable for quantifying representative track lengths or annealing behaviors.

Thank you for recognizing the significance of selecting 80 MeV Xe ions for this study. We believe that the TEM images of the ion tracks produced by 80 MeV Xe ion irradiation are valuable in their own right. On the other hand, we acknowledge that the 300 MeV Kr ions used by Weise et al. (2009) do not represent typical fission-fragment energies, as they also state in their paper. We will add clarification to the introduction stating that our present work is the first to investigate FT annealing in monazite using energies that closely mimic those of natural fission fragments. However, we will retain the citation for this previous study as it was pioneering work on the FT annealing process in monazite involving ion tracks, despite the much higher energy.

>Conventional TEM imaging (Figs. 1–3) cannot definitively confirm crystalline structure retention within monazite tracks. Obtaining high-quality cross-sectional HRTEM images of ion tracks demands precise mutual alignment of three axes: the ion irradiation direction, a low-index zone axis of the matrix, and the electron beam. Without this strict alignment, lattice fringes observed "on top" of tracks may misleadingly originate from the overlapping crystalline matrix rather than the track core itself. Consequently, HRTEM combined with FFT or SAED is necessary to rule out such alignment artifacts. Furthermore, because amorphous features in beam-sensitive minerals like monazite and apatite are easily obscured by electron-beam-induced damage, amorphous tracks are far more difficult to detect than intact lattice fringes. The authors must demonstrate that beam damage was minimized during sample tilting/observation and contextualize these local observations with more reliable bulk characterizations of amorphization, such as Raman spectroscopy and XRD (e.g., Overstreet et al., NIMB 2022).

Strictly speaking, conventional TEM imaging is not sufficient to precisely determine the crystalline structure or crystalline symmetry of an ion track, whereas HRTEM is suitable for this purpose, provided that the mutual alignment of the three axes is precisely controlled. However, conventional TEM imaging is sufficient to identify whether the ion tracks are fully amorphous or not. In this case, precise alignment of the three axes is not as critical.

For example, the thickness of a TEM specimen is typically less than 100 nm, whereas the diameter of an ion track is approximately 10 nm. Even if the specimen is tilted by as much as

5 degrees, which is quite a large misalignment, it is still possible to observe a portion of the ion track that is not overlapped by the surrounding matrix. (Furthermore, we are confident that the actual misalignment in our experiments is far smaller than 5 degrees.) Therefore, such a misalignment does not prevent us from determining whether the ion tracks are fully amorphous. Indeed, in our observation ion tracks in zircon can be clearly imaged as amorphous regions, while the ion track images obtained from monazite are found to be distinctly different from those observed in zircon.
Nevertheless, in response to the reviewer's concern, we will qualify our TEM observations by stating that they indicate "no detectable complete amorphization" rather than an absolute absence of amorphous materials. We will add a statement acknowledging the limitations of conventional TEM and the need for HRTEM, FFT, or SAED.

>Line 20: Describing tracks as "low-density regions" (rather than asserting that "crystalline structure is retained") is scientifically safer until HRTEM evidence confirms the absence of amorphous components.

We agree that the expression "crystalline structure is retained" may be misleading, as it could be interpreted to mean that the original crystalline structure of the ion tracks is fully preserved and remains intact. This was not our intention, and we will revise the wording accordingly. In the revise manuscript, "crystalline structure" or "crystalline tracks" were replaced by "low-density regions", based on the current resolution limits of our TEM data.

>Line 61: While a significant amount of heat is generated by gamma-ray release during neutron absorption by the high Gd content in monazite, potentially reaching temperatures high enough to melt the sample, it is scientifically inaccurate to frame this mechanism as "thermal neutron shielding" since the overall proportion of absorbed neutrons remains extremely low.

The cited paper, Gleadow et al. (2002), described neutron self-absorption during neutron irradiation. In the abstract of Gleadow et al. (2004) of the Goldschmidt conference, they described that the REEs, particularly Gd and Sm, cause neutron self-shielding. The phrase "thermal neutron shielding" will be replaced by "thermal-neutron capture with subsequent gamma ray emission", and will also cite Jones et al. (2021) for the Gd thermal-capture cross-section.

>Line 76: Define the acronym "TEM" (Transmission Electron Microscopy) upon its first use to improve readability.

The abbreviation TEM will be defined at its first occurrence.

>Line 82: Monazite tracks appear to align with the “intermediate type” damage (discontinuous droplets or low-density domains) observed in TiO2 (Zhai et al., NIMB 2019) and CeO2 (Takaki et al., Prog. Nucl. Energy 2016), rather than being purely crystalline. While ion tracks are widely considered amorphous in most materials (including zircon, pyrochlore, quartz, and epidote), the authors should contextualize these observations within the wider thermochronology literature. For instance, apatite exhibits highly porous tracks, as demonstrated by HRTEM, Fresnel contrast, and thermal annealing studies (Li et al., PRB 2010). Because the tracks in the authors' monazite samples exhibit discontinuous droplets and low-density areas, classifying them as this "intermediate type" would be much more accurate.

We will add some explanations the observed low-density domains of monazite tracks within the “intermediate type” damage category reported for TiO_2 and CeO_2. The comparison with apatite HRTEM studies will be also included.

>Line 87: The repetitive use of “lead to” makes the sentence awkward. Revise for clarity.

We will remove the second “leading to” and just put “and”.

>Line 115: The text states that irradiations were performed “perpendicular to the grid surface,” but Figure 3 displays a 45° tilt. Please clarify in the Methods section that some grids were tilted pre-irradiation.

We thank the reviewer for pointing out this inconsistency. The method section will be revised to state “Irradiations were performed with the specimen grid either perpendicular to the beam or tilted by 45° .

>Line 120: Note that Weise et al. (Chem. Geol. 2009) used 300 MeV ions, which exceed both single fission fragment energy (~70–100 MeV) and total fission energy (~170 MeV). In contrast, Li et al. (EPSL 2012) correctly used a representative 80 MeV Xe ion beam for single-fragment simulation.

We are sorry for misleading you with these explanations. Weise et al. (2009) provided the nuclear track properties of the light and heavy particles from spontaneous fission events in Table 2, and then we cited the parameters of that. We will refine this sentence to prevent misunderstanding.

>Line 125: This section omits critical chemical etching details (e.g., 6M HCl at 90° C,

per Jones et al., Terra Nova 2019). Explicitly state these experimental parameters.

The chemical etching protocol will be restated here, as well as the Method section.

>Line 135: The absence of visible amorphous features under conventional TEM does not prove their total absence within the tracks; stringent imaging orientation requirements and electron-beam damage can easily obscure small, localized amorphous domains.

The sentence at Line 135 will be refined as follows: "In the magnified image of the irradiated domains, no detectable amorphous domains were observed at both energies. The formation of low-density domains implies the formation of atomic vacancies, e.g., point defects, within the crystal lattice, instead of amorphization."

>Line 140: In monazite, 80 MeV Xe ion tracks are discontinuous from the initial stage of penetration, contrasting with apatite where tracks remain continuous until near the terminal range (Li et al., EPSL 2012). Furthermore, during annealing, continuous apatite tracks segment into discontinuous droplets driven by Rayleigh instability. This divergent behavior demonstrates that continuous, heavily damaged zones develop more readily in apatite than in monazite under identical irradiation conditions.

A comparative paragraph will be added: "Monazite tracks produced by 80 MeV Xe ions become discontinuous already in the early penetration stage, whereas apatite tracks remain continuous until the near-terminal range (Li et al., 2012). Upon annealing, continuous apatite tracks fragment into droplets via Rayleigh instability, indicating a greater propensity for the accumulation of extensive damage compared with monazite. "

>Figures 1–4: The authors reported circular tracks in zircon (Figure 4) yet rectangular ones in monazite (Figure 1). However, latent track geometry is highly sensitive to the ion's trajectory relative to the crystal lattice, necessitating a precise determination and reporting of the crystallographic orientation of the irradiated crystals. For instance, Li et al. (Am. Mineral. 2014) demonstrated via HRTEM and conventional TEM that ion tracks in zircon can appear oval or rectangular, rather than strictly circular, depending on the irradiation direction. Consequently, the circular morphology presented in Figure 4 may simply reflect a specific crystallographic section or imaging condition rather than an intrinsic, isotropic track structure.

We conducted TEM observations on the crashed fragments of monazite and zircon crystals, rather than resin-mounting or fixing a crystal to expose the target crystallographic orientation, thereby yielding a random crystallographic orientation. We will add to state: "Ion tracks were observed on randomly oriented crystal fragments. Since ion tracks in zircon can exhibit either oval or circular morphologies depending on the crystallographic orientation, the circular morphology observed in this study may reflect the particular crystallographic section examined rather than an inherently isotropic track geometry." No further speculation on the origin of the shapes will be made.

>Line 181: The attribution of "enhanced etching resistance" in Toya-6b to "minimal radiation damage" lacks a mechanistic explanation. The authors should expand on the physical basis for this relationship—specifically, how a low baseline of cumulative damage reduces defect density or chemical reactivity (e.g., Nakajima et al., GChron 2024). Clarifying whether this resistance arises from reduced preferential leaching along damaged zones versus changes in bulk dissolution kinetics would strengthen the interpretation.

Nakajima et al. (2024) reported that natural monazite crystals with lower radiation damage (namely, Toya-5b) exhibited greater resistance to bulk-crystal etching, as indicated by Raman spectroscopy and step-etching experiments. In this context, we will propose that the etching resistance reduces where ion particles penetrate. We will add the sentence before Line 183: "Nakajima et al. (2024) showed that low radiation damage monazite exhibits longer etching duration with comparison between various natural monazite, as confirmed by Raman spectroscopy and step-etching experiments. They concluded that monazite with lower radiation damage yields higher bulk dissolution resistance "

>Line 187: Overstreet et al. (NIMB 2022) identified amorphous components in Sm/Tb-monazite via TEM/XRD/Raman, even when lattice fringes remained visible in conventional TEM, proving that misalignment can mask amorphous cores. Because GeV ions possess a comparable electronic stopping power (Se) to actual fission fragments, their energy range alone does not invalidate their findings.

In our opinion, a comparative study of amorphizable zircon and (possibly) non-amorphizable monazite should be conducted by Overstreet et al. to demonstrate whether significant misalignment of the TEM sample occurs during the experimental procedure. If the ion tracks in zircon are observed under the same imaging conditions, lattice fringes should also be visible within the zircon ion tracks. In contrast, in our observations, lattice fringes are absent from at least the majority of the ion tracks. Nevertheless, we agree that additional techniques are necessary to definitively demonstrate that an amorphous phase is indeed formed within the ion tracks.

Therefore, we will revise the entire discussion of Section 4.1 based on your major comments. A new sentence will also be added at the last sentence of the first paragraph: “Consistent with Overstreet et al. (2022), our conventional TEM observations cannot exclude the presence of amorphous cores; bulk techniques such as Raman or XRD are required for definitive confirmation.”

> Line 220: The absolute statement “no amorphization” should be revised to “no complete amorphization” or “no metamictization,” strictly following the cited reference (Nasdala et al., Sci. Rep. 2020).

All instances of “no amorphization” have been replaced by “no complete amorphization”.

> Line 230: While helium ion irradiation experiments show radiation damage at low accumulation thresholds (Nasdala et al., Sci. Rep. 2020), it is mechanistically incorrect to attribute natural alpha-particle accumulation as the primary driver of track damage. Alpha-recoil nuclei are the dominant drivers of radiation damage in natural samples, whereas alpha particles themselves primarily promote electronic ionization and structural healing.

We will revise the sentence at Line 230 and will add the explanation: “Natural α-recoil nuclei are the primary source of lattice damage in monazite, whereas α-particles mainly induce electronic excitation and can promote local annealing; therefore, attributing track damage primarily to α-particle accumulation is mechanistically inaccurate.”

> Line 243: Lithium fluoride is highly sensitive to electron beam irradiation, which can rapidly induce amorphous artifacts across both the matrix and track zones. Consequently, conventional TEM makes it difficult to precisely isolate the presence of amorphous tracks, because remaining crystalline structures generate strong diffraction contrast that overpowers the amorphous signal. Even if amorphous features are not directly observed at the top of the damaged region in LiF via TEM, concluding that the tracks fundamentally lack amorphous components is scientifically unjustified.

In this context, we discussed that the ion tracks could be etched even if no amorphous signatures were observed, because it is well established in fission-track thermochronology that amorphous regions could be etched selectively due to enhancing the etching rate. We will consider logic and revise, including removing the previous etching experiment using ion tracks on LiF.

>Line 265: Individual point defects cannot be resolved via conventional TEM. Soften claims such as “point defects are present” to “damage likely includes point defects.”

The claim “point defects are present” will be softened to: “Damage likely includes point defects, although they cannot be directly detected by conventional TEM”

>Line 300: The closure temperature of fission tracks in minerals is dictated by a complex interplay of factors, including track geometry, the structural state of the damaged core, the thermal response of the damage zone, and chemical interactions between the damaged volume and the host crystalline matrix. The authors are encouraged to expand their discussion to explain why monazite exhibits an even lower closure temperature than apatite.

Section 4.3 will be expanded to discuss a comparison of various factors between mineral species (e.g., apatite, zircon, monazite), including those you suggested.