Comments by referees are in blue.

Our replies are in black.

Changes to the manuscript are highlighted in red both here and in the revised manuscript.

Reply to referee #1

This paper provides a comprehensive summary of iron isotopes in aerosols, including analytical methods. Each paper is carefully read and explained, but I believe further discussion is necessary to integrate the findings more cohesively.

Reply: We would like to thank ref#1 for recommending our manuscript for publication and his/her comments which have help us further improve our manuscript. We have addressed these comments and updated the manuscript accordingly; when we do not quite agree with ref#1, we have provided proper explanation. Please find more details below.

For example, a more comprehensive discussion could be achieved by taking into account previous data, such as (i) differences in δ56Fe endmembers among different papers and (ii) the extent to which isotope fractionation caused by chemical processes in the atmosphere actually alters the δ56Fe composition of soluble iron in aerosols.

Reply: For studies which measure isotopic composition of aerosol Fe in the atmosphere, the authors normally chose endmember values which can best explain their measurement (typically the lowest δ^{56}Fe they measured in a given study). We are not sure whether and to which extent comparison of endmember values used in different studies can help. This is why we use Section 3.2 to discuss previous studies which reported δ^{56}Fe for aerosol Fe from different sources.

Very few studies which measured δ^{56}Fe in the atmosphere considered isotopic fractionation, and the extent to which isotope fractionation caused by chemical processes in the atmosphere actually alters δ^{56}Fe of soluble aerosol Fe is far from being understood. However, Conway et al (2019) showed no isotopic fractionation of the soluble Fe when looking at aerosols collected near the Sahara. This is a topic which should be considered in future work, as we underscore in the perspective (Section 4). This is also why we use Section 3.5 to discuss previous laboratory studies which examined isotope fractionation. To make it clearer, in the revised manuscript (page 29) we have made the following change to the first paragraph of Section 3.5: "Chemical processes which change the speciation of Fe in the environment may also lead to isotopic fractionation (Table S1), and thereby may attenuate Fe isotopic signatures observed in ambient aerosols. However, when using Fe isotopic composition to trace sources of total and soluble aerosol Fe, only a few studies have discussed possible Fe isotopic fractionation induced by atmospheric chemical processing (Labatut et al., 2014; Camin et al., 2024); most previous studies assumed that total and soluble Fe from a given source have the same endmember value, implicitly assuming no Fe isotopic fractionation. On the other hand, Conway et al. (2019) showed that total, water-soluble and seawater-soluble Fe in Saharan dust aerosol over the North Atlantic all had the equivalent δ^{56}Fe to the UCC, suggesting no Fe isotopic fractionation and supporting the use of endmembers without fractionation."

Additionally, I suggest reconsidering the structure of the manuscript. For example, some of the discussions in each subsection in Section 3 are only summaries of the other subsections or continuation of explanations; it would be more effective to create a separate discussion section to provide a more comprehensive synthesis.

Reply: We respect but do not quite agree with this comment. We have Sections 3.2.4, 3.3.3 and 3.5.5 to summarize Section 3.2, 3.3 and 3.5, respectively. We feel that they are very necessary, because 1) the contents presented in Sections 3.2, 3.3 and 3.5 are very rich; 2) Section 3.2, 3.3 and 3.5 are focused on different aspects. For example, summarizing and discussing what is known for endmembers values (Section 3.2.4) helps us discuss each papers in Section 3.3 (Fe isotopic composition of ambient aerosols).

Also, the same references appear several times in one paragraph, making it difficult to read, and it would be better to reduce such redundancies.

Reply: It is a good suggestion. In the revised manuscript we have tried our best to reduce such redundancies if this does not reduce the clarity.

Specific points are described below:

L. 111: It is unclear what "marine source materials" means.

Reply: It means potential sources of Fe to the ocean. In the revised manuscript (page 6) we have made the following change to make it clearer: "this parameter has been measured both in potential source materials of Fe to the ocean (Beard et al., 2003a), and later in seawater itself…"

L. 136: Please spell out the "IRMM" at first mention.

Reply: As suggested, in the revised manuscript (page 7) we have defined IRMM: "…reported relative to the IRMM-014 standard (provided by the Institute for Reference Materials and Measurements, IRMM)…"

Section 2.2: I suggest adding information on the required Fe amount for TIMS measurement and the purification method for MC-ICP-MS analysis.

Reply: To provide information on the required Fe mass for TIMS measurement, in the revised manuscript (page 7) we have made the following change: "In early works, TIMS was combined with the double-spike technique, requiring a minimum Fe mass of >1 μg and yielding precision of ±0.5‰…"

Since Fe isotopic analysis is not a focus of our review paper, we only mention its key aspects and do not discuss details. Instead of providing a detailed description of Fe purification, in the revised manuscript (page 8) we have added one sentence to refer readers to literature: "…samples must be cleanly purified from interfering isobars (Cr and Ni) and matrix elements (e.g., Ca), and further information on Fe purification can be found elsewhere (Conway et al., 2013; Sieber et al., 2021)."

L. 179: Please include the procedural blank value.

Reply: In the revised manuscript (page 9) we have included information for the procedural blank: "a concentration that is >20-40 times of our chemistry procedural blank which is typically <0.5 ng/g."

L. 188-191: I recommend moving this paragraph to another subsection within Section 2 and providing further explanation regarding aerosol sample processing, including sampling, acid digestion, extraction procedure, and so on. Otherwise, the explanation seems a bit abrupt.

Reply: We agree that in our original manuscript this short paragraph appears to be abrupt, because its connection with previous paragraphs (which are focused on instrumental analysis) is not very clear. As a result, we have made the following change in the revised manuscript (page 9): "In addition to instrumental analysis, a further consideration for aerosol samples that often include significant filter or digestion blanks is the blank isotopic composition…"

Instead of providing further details on aerosol sampling, processing, and so on, in the revised manuscript (page 9) we have added two references (Kurisu et al., 2024; Bunnell et al., 2025) from which interested readers can find more information.

Section 3.2: It would be more effective to summarize previous aerosol δ56Fe results in a figure.

Reply: Two previous review articles (Wang et al., 2022; Wei et al., 2024) provide figures similar to what referee #1 suggested. As a result, we choose to provide a comprehensive compilation of results reported in individual studies (Table S1), instead of using a figure similar to those which can be found in elsewhere.

Table S1 and S2: Please add more information such as: (1) A simple explanation of the sample (e.g. whether it was collected near specific sources or in urban/suburban areas); (2) Soluble Fe extraction method (if available); (3) If it is a certified reference material, the name of CRM.

Reply: Here ref#1 has three comments, and they are addressed below.

1) Tables S1 and S2 summarize source materials and ambient aerosols, respectively, and thus we feel the explanation ref#1 suggested is not necessary.

2) It is difficult to add another column into one of the two tables, and therefore we decide not include soluble Fe extraction method in these two tables. Instead, we have include an appendix in the revised manuscript (page 36-37) where we define and discuss total and dissolved Fe (and also several other terms).

3) Usually each individual study included in Table 1 examined more than one sample, and we provide the range and the average for each individual study; as a result, it is not possible for this table to provide the names of CRM used.

In summary, although it would be nice to provide additional information in Tables S1 and S2, we can only provide key information in these tables due to space limit.

L. 259: Biomass burning is not mentioned in Section 3.2.3.

Reply: We agree with ref #1, and have made the following change in the revised manuscript (page 12): "…and aerosol particles emitted by various anthropogenic sources (Section 3.2.3)."

L. 262: This sentence could be omitted.

Reply: We would like to keep this sentence, as this sentence informs the reader the content of Section 3.2.1 in a concise way.

L. 302~: An explanation of Strategies I and II is necessary here.

Reply: It is a good suggestion. In response to this comment, in the revised manuscript we have provided explanation of strategies I and II plants in the appendix (page 36-37).

L. 313~: I found it unclear that Strategy I is isotopically lighter than Strategy II; it rather appears that Strategy II yields lower δ56Fe values. This might be due to δ56Fe being shown as a range. Please consider a more effective way for a clearer explanation. In addition, the reasons for the different δ56Fe values between Strategies I and II should be included.

Reply: The referee raised a very good point. Indeed the ranges we provide in the original manuscript seem to suggest Fe in Strategy II plants are lighter. Unfortunately the paper by Kubik et al. (2021) only presents the data graphically, and it is not possible to obtain average or median values. As a result, in the revised manuscript we have removed this sentence (which presents δ^{56}Fe ranges for Strategy I and II plants) to avoid confusion. In the revised manuscript we have added one sentence to explain why δ^{56}Fe are different for strategy I and II plants. We incline to keep this explanation very short and refer interested readers to literature, because our review article is focused on isotopic composition of aerosol Fe (rather than plant Fe).

To summarize, in the revised manuscript (page 15), the discussion of the work by Kubik et al. is given below: "Kubik et al. (2021) surveyed Fe isotopic compositions of biological samples and found that in general Fe in strategy I plants is isotopically lighter than strategy II plants. This is because strategy I and II plants use different biochemical mechanisms to absorb Fe from soil (Kubik et al., 2021)."

L. 324~: This paragraph may be unnecessary.

Reply: This paragraph summarizes Section 3.2.3, and more importantly, it points out that Fe isotopic composition is not necessarily identical for source materials and aerosol particles emitted. As a result, we feel that it is necessary and would like to keep it.

L. 330: I found the title "anthropogenic aerosols" unclear; the relationships among Sections 3.2.2, 3.2.3, and 3.3 were not obvious. I understood that 3.2.3 describes materials that can be atmospheric anthropogenic aerosols. Therefore, I suggest changing the title to something like "Materials that can be emitted as aerosol particles" or simply "fly ash and road dust". It would also be beneficial to review the structure of 3.2.2 and 3.2.3 to determine which discussion should be in the same section or not. Combining the two sections into one would be another option.

Reply: We agree that the title of Section 3.2.3 in our original manuscript is somehow unclear, and in the revised manuscript (page 15) we have changed it to "Aerosol particles emitted by anthropogenic sources".

It may be an alternative option to combine Sections 3.2.2 and 3.2.3. Nevertheless, we would like to keep them separated because (1) these two sections discuss different contents (although related) and (2) if we combine Sections 3.2.2 and 3.2.3, the section we obtain will be very long.

L. 353~: This paragraph may not be necessary or could be simplified.

Reply: This paragraph summarizes what we present in the previous paragraphs and sets the background for the following paragraph; as a result, we think it is necessary. This paragraph only contains two sentences and is not long. As suggested by the referee in previous comment. in the revised manuscript we have deleted unnecessary reference in this paragraph to increase its readability.

L. 380~: As mentioned earlier, this section would be better placed in Section 4 or another discussion section.

Reply: Section 3.2.4, which has about 20 lines, summarizes and discusses what we present in Section 3.2, and therefore we would like to keep it at the end of Section 3.2. Indeed a more concise summary (line 777-784, only 8 lines) can be found in Section 4.

L. 406: The meaning of "total" should be clarified, such as by stating "total (acid digested)."

Reply: As suggested, we have added one appendix in the revised manuscript (36-37) to define discuss several terms, including total and dissolved Fe.

L. 409: It may be more effective to organize sections based on a different perspective (e.g., sampling location (land or ocean) or particle size separation) rather than publication year.

Reply: We have thought about organizing published studied in different ways. It is possible to organize these studies based on sampling location (land or ocean); nevertheless, aerosol Fe does not have marine sources, and it may not help much to organize these studies based on whether sampling was taken over the ocean or land. If we organize these studies based on particle size, it makes comparison of Fe isotopic compositions of different sizes less direct. At the end, we choose to organize them based on publication years.

L. 425: PM should be spelled out.

Reply: We agree with the referee. In response to this comment, in the revised manuscript (page 36-37) we have defined $PM_{2.5}$, $PM_{<2.5}$ and PM_{10} in the appendix.

L. 529: The endmember values should be mentioned.

Reply: In the revised manuscript (page 23-24), we have made the following change to mention the endmember values Kurisu et al. used: "…the relative contribution of combustion to total aerosol Fe could be up to 50% and 6% for fine and coarse particles, assuming δ^{56}Fe endmember values to be +0‰ and -4.7‰ to -3.9‰ for dust and combustion Fe."

L. 534: Please clarify whether there is a difference between "fine (<2.5 μm) particles" and PM2.5, and unify the terminology.

Reply: Fine and coarse particles are general terms which are vague to some extent. There is no consistent definition of fine and coarse particles, and the cutoff size vary around slightly <1 μm to >2.5μm in different studies. That is why in our manuscript we always try to specify the size range when possible (for example, $PM_{2.5}$, PM_{10}, >2.5μm, and etc.).

L. 545: -1.87 and +0.28 should be rounded to -1.9 and +0.3, aligned with "-0.5 to +0.4‰".

Reply: As suggested, in the revised manuscript (page 24) we have changed it to "from -1.9 to +0.3‰".

L. 580: As mentioned above, please reconsider the position of this section, and reduce the number of references cited within the same paragraph for better readability.

Reply: As suggested, in the revised manuscript we have tried our best to reduce the number of cited references for better readability. Section 3.3.3 summarizes what we present in Sections 3.3.1 and 3.3.2, and therefore we think that it is placed in the right place.

L. 626: Mead et al. (2013), Kurisu et al. (2016), and Li et al. (2022) report δ56Fe values of coal fly ash but do not claim that the heavy δ56Fe in aerosols originates from coal fly ash. Thus, this citation may be inappropriate. It should also be cited that heavy δ56Fe may result from isotopic fractionation in the atmosphere (Labatut et al., 2014; Camin et al., 2024).

Reply: Indeed the three studies (Mead et al., 2013; Kurisu et al., 2016; Li et al., 2022) support but do not make the claim that heavy δ^{56}Fe in aerosols originates from coal fly ash. In the revised manuscript (page 27) we have removed these three references and made the following changes: "This observation has been variably attributed to coal and oil fly ash, to wildfire emissions (Bunnell et al., 2025), or to Fe fractionation due to chemical processing in the atmosphere (Labatut et al., 2014; Camin et al., 2024)."

L. 642: "IMPACT" model should be spelled out.

Reply: As suggested, in the revised manuscript (page 28) we have provided the full name of the model: "Kurisu et al. (2021) employed the integrated massively parallel atmospheric chemical transport (IMPACT) model…"

L. 646: Kurisu et al. (2021) suggests the underestimation of mineral dust in coarse particles by the model as well as the inappropriate endmember value of anthropogenic Fe.

Reply: We agree with the referee. In fact this has already by discussed in our original manuscript (line 647-650), where it is stated "if the endmember δ^{56}Fe value of combustion Fe was set to be larger for coarse particles than fine particles, the model may reproduce the observed δ^{56}Fe for both fine and coarse particles."

L. 692: Please verify whether the fractionation factor cited here is appropriate. Skulan et al. (2002) suggest the kinetic isotope fractionation factor of hematite precipitation as +1.32‰, meaning the dissolved phase becomes heavier. They also suggest that there is no clear fractionation during the dissolution experiment with 0.9 mol/L HCl.

Reply: As suggested, we checked the paper by Skulan et al. (2002) carefully, and agree with the referee that our initial interpretation was incorrect. In the revised manuscript (page 30), we have made the following change: "For hematite dissolution in 0.9 mol/L HCl, no significant equilibrium fractionation of Fe was observed (Skulan et al., 2002)."

L. 700: This part may be unnecessary. Since the conditions of each experiment are different in terms of mineralogy, temperature, solvent, equilibrium/kinetic, etc., it is understandable that the degree of fractionation varies.

Reply: We agree with the referee that this paragraph is not very necessary. As a result, we have deleted it in the revised manuscript.

L. 745: The title of this section should be revised, as it is not a discussion in response to the previous section, but simply describes an experiment under real atmospheric conditions.

Reply: We agree with the referee. In the revised manuscript (page 32) we have changed the title of Section 3.5.4 to: "Fe isotopic fractionation caused by atmospheric chemical processing".

L. 755: Consider explaining the dissolution rate (%) rather than dissolution time, as it would facilitate comparisons with other studies.

Reply: As some other studies did not report dissolution fractions, it is difficult to compare different studies based on dissolution fractions. However, what ref #1 suggested is very good, and in the revised manuscript (page 35) we have added one sentence to recommend this for future work: "We suggest that dissolution fractions (in %) should also be reported together with isotopic fractionation, in order to facilitate comparisons between different studies."

L. 784: Could you clarify what kind of experimental measurements you expect? I believe this is an important perspective that should be addressed.

Reply: As suggested, in the revised manuscript (page 34) we have modified this sentence to make our recommendation more explicit: "Therefore, measurements of size-dependent δ^{56}Fe of total and soluble Fe in aerosol particles emitted by various anthropogenic and combustion sources are highly recommended."

L. 798-800: Based on the discussion in Section 3.5, if isotopic fractionation of Fe aerosols in the atmosphere is driven by chemical processes, a relationship between solubility and isotopic fractionation (difference between total and soluble) should exist — i.e., lower solubility corresponds to larger isotope fractionation. I am curious whether such a relationship can be identified from the compiled data. This discussion should address whether the low δ56Fe in soluble Fe is due to different sources or chemical processes.

Reply: We think that both sources and chemical processes will influence isotopic composition of total and soluble Fe. However, their relative extents are totally unclear ambient aerosol Fe, since most previous studies on aerosol Fe isotopes did not consider Fe isotopic fractionation. This is exactly why we use Section 3.5 to discussion Fe isotopic fractionation induced by chemical processing (we also discuss this issue in Section 4). We hope that this will stimulate future studies to take into account the effects of Fe isotopic fractionation on isotopic composition of aerosol Fe in the atmosphere.