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 #2

Several comments from referee #2 are closely related, so we have grouped and addressed them together. Please note that the order of some comments is thus different from that in the original review.

General comments

The stable isotope ratio of Fe has been used for source apportionment of total and soluble aerosol Fe. However, there are still large uncertainties in the δ56Fe endmember values for aerosol Fe from various sources. The authors collected and measured δ56Fe for fly and bottom ash samples. The measurements conducted in this study might contribute to a better understanding of the mechanisms of isotopic fractionation. However, the misuse of the heavy δ56Fe endmember values for fly ash samples would contradict observational facts. Moreover, the caveats in recommendations for future work and conclusion should be carefully considered for the interpretation in the main text. Major revisions are needed before this manuscript can be considered for publication in ACP.

Reply: We woud like to thank ref #2 for reviewing our manuscript, recognizing its significance and recommending it for publication after major revision. We have carefully addressed these comments which significantly help us further improve our manuscript, and revised the manuscript accordingly. For more details, please kindly refer to our response (as shown below) to specific comments.

Major comment

Please clarify that the heavy δ56Fe samples are captured as large particles before the emission into the ambient atmosphere. Additionally, please measure δ56Fe for the raw materials (except biofuel burning) and for actual aerosols in the ambient atmosphere to suggest the use of δ56Fe endmember values for the ambient aerosols, and discuss the mechanisms of isotopic fractionation. Since these isotopically heavy Fe aerosols (except biofuel burning) are captured or retained before being emitted to the atmosphere, the actual aerosols in the ambient

atmosphere could be lighter, as the volume mean diameters of fly ash samples are mostly a few tens of μm, which are considerably larger than those for submicron aerosols with light δ56Fe. Please reconsider the interpretation throughout the manuscript.

l.404: Previous studies used δ56Fe for the aerosols in the ambient atmosphere, not assumed δ56Fe captured before being emitted into the atmosphere. Since these isotopically heavy Fe aerosols as large particles cannot be emitted to the atmosphere owing to the emission control devices, the actual aerosols in the ambient atmosphere can be lighter. Please discuss the mechanisms of isotopic fractionation.

Reply: The two comments above are closely related, and therefore they are addressed together. Our response to these comments is organized around three main themes, as detailed below.

1) Caveats of our work

Indeed power plant coal fly ash and steelwork fly ash samples we used are mainly large particles. As suggested, in the revised manuscript we have added one sentence to provide size information for power plant coal fly ash (page 6): "These samples were obtained from baghouse rows or electrostatic precipitators in coal power plants (Li et al., 2026), and their volume equivalent diameters were in the range of 16.9-67.6 μm (Table S3)." Another sentence has been added for steelwork fly ash (page 6): "The 21 steelwork fly ash samples (Table S4) were provided by large and medium-sized steelwork plants located in different regions in China (Li et al., 2026), and their volume-equivalent diameters were in the range of 4.6 to 176.4 μm (Table S4)."

We acknowledge that fly ash samples examined in this work may not fully represent atmospheric aerosol particles, as we discussed in our original manuscript (Sections 3.4.2 and the last paragraph in Section 4). In the revised manuscript, we have changed the title of Section 3.4.2 from "Recommendations for future work" to "Caveats and limitations" (page 20), in order to present a more balanced assessment of our findings. We have also revised Section 3.4.2, to further discuss the isotopic fractionation mechanisms and the caveats of our work (please see below).

Moreover, in Section 4 (Conclusion and recommendations for future work) of the revised manuscript (page 22), we have added the following sentence to mention the caveats of our present work: "It should be mentioned that fly ash samples used in our current work may not

be fully representative of aerosol particles emitted into the atmosphere by coal-fired power plants and steelwork plants."

2) The discussion of isotopic fractionation mechanisms

In our original manuscript we discussed Fe isotopic fractionation mechanisms (Section 3.4.2, page 20). In the revised manuscript (page 20), the title of Section 3.4.2 has been changed to "3.4.2 Caveats and limitations" to better reflect its content. We have also added one sentence to further discuss the mechanisms of isotopic fractionation: "Lighter Fe preferentially evaporates at high temperatures and subsequently condenses to form Fe-containing nanoparticles, and thus particles with smaller size will be enriched in lighter Fe (Kurisu et al., 2016b; Kurisu et al., 2019)."

When addressing the comments raised by referee #2, we have closely looked at our data and realized that for steelwork fly ash samples we examined (18 samples in total), 7 samples were actually aerosol particles emitted into the atmosphere (we were aware of these samples, but had not paid enough attention). Fe in the 7 aerosol samples was not isotopically lighter than the 11 fly ash samples, but we note that this is not necessarily incompatible with the Fe fractionation hypothesis. Accordingly, we have added one paragraph in the revised manuscript (page 21) to further discuss our data and the Fe fractionation hypothesis: "Among the 18 steelwork fly ash samples we examined (excluding the three coking fly ash samples), 11 samples were fly ash particles retained in dust collectors, with δ^{56}Fe in the range of -1.11‰ to +0.20‰; the other 7 samples were aerosol particles emitted into the atmosphere (the last seven samples in Table S4), with δ56Fe in the range of -1.16‰ to +0.29‰. Fe in the 7 aerosol samples was not isotopically lighter than that in the 11 fly ash samples retained by dust collectors. Nevertheless, this is not necessarily incompatible with the Fe fractionation hypothesis, because these samples were not collected from a single plant and the variation of δ56Fe in raw materials may also play a role."

3) Recommendation for future work

We agree that it would be informative to measure δ^{56}Fe values for both the raw materials and the corresponding aerosol samples. Nevertheless, this would require a large amount of additional experimental work and is therefore beyond the scope of the present study. First, the fly ash samples used in this work were collected from various plants by different individuals and at different times, making it impractical to obtain the corresponding raw materials and aerosol samples. Second, Fe isotopic measurements are costly, and our dataset comprises 84

individual δ^{56}Fe measurements, substantially larger than those reported in most previous studies.

Nevertheless, referee #2 did raise an excellent point regarding future work. In response, we have expanded our recommendations for future research in the revised manuscript to better understand Fe isotopic fractionation during high-temperature processes and δ^{56}Fe values for anthropogenic aerosol Fe, as detailed below:

(i) Page 22: we have changed the title of Section 4 from "Conclusion" to "Conclusion and recommendations for future work", in order to better reflect the content presented this section.

(ii) Page 23: we have added the following sentence at the beginning of the fourth paragraph: "We acknowledge several caveats in our study, and outline recommendations for future work to address them.", to clearly articulate the purpose of this paragraph and the one that follows.

(iii) Page 24: furthermore, we have implemented the following change (page 24) in the last paragraph to further elaborate on our recommendations for future work: "Experimental measurements of δ^{56}Fe values for aerosol particles emitted by anthropogenic sources would be very valuable in providing reliable constraint on δ^{56}Fe endmember values. For a given anthropogenic source (e.g., a coal-fired power plant or a steel plant), ideally one would measure isotopic compositions of Fe in raw materials, fly ash retained by dust collectors, and the size-resolved aerosol particles emitted to the atmosphere. Such measurements will further help to constrain whether, and to what extent, evaporation-condensation during high-temperature processes induces Fe isotopic fractionation."

Summary: In response to these two comments, we have further clarified the caveats of our present work, reinforced our discussion on the Fe isotopic fractionation hypothesis, and refined our recommendations for future work. These revisions have substantially enhanced the quality of our manuscript, rendering it more insightful and better balanced (in weighing significance and evidence against potential limitations).

Please separate the discussion of δ56Fe between biofuel burning and open biomass burning, as aerosol Fe during open biomass burning is mainly derived from soil-suspended particles.

l.334: Even though domestic biofuel burning may not be representative of wildfires, why did you compare it with open biomass burning? Please reconsider the interpretation to explain the meaning of the comparison throughout the manuscript.

l.385: Please separate the discussion between biofuel burning and open biomass burning.

Reply: The three comments above are closely related, and therefore they are addressed together.

On one hand, we agree with ref #2 that biofuel and open biomass burning aerosols are different. On the other hand, we would like to point out that the two types of aerosols are also closely related. This is why these two types of aerosol Fe are sometimes discussed together.

As we stated in our original manuscript (line 398-399), soil and biomass Fe both contribute to aerosol Fe emitted by open biomass burning. As a result, open biomass burning aerosol Fe carries isotope signatures of both soil Fe and biomass Fe. The δ^{56}Fe values measured in this work for biofuel burning aerosol are also relevant for, although not fully representative of, open biomass burning aerosol Fe. This is why we discussed the relevance of our work for open biomass burning aerosol Fe (the first paragraph of Section 3.3.3 and the first paragraph of Section 3.4.1).

We do acknowledge that biofuel burning aerosol Fe is not identical to open biomass burning aerosol Fe. This is why in the second paragraph of Section 3.4.1 (line 396-401) we point out that wildfire aerosol Fe may have δ^{56}Fe endmember values different from that we report for domestic biofuel burning aerosol.

To address these three comments and further clarify our discussion and interpretation (for example, to emphasize the difference between biofuel burning and open biomass burning), we have made the following change in our revised manuscript (page 19): "Therefore, the δ^{56}Fe signatures of wildfire aerosol Fe likely reflect a mixture of soil and biomass endmembers, distinct from those we reported for domestic biofuel burning."

Specific comments

l.122, l.128, and l.168: Please explain the size and collection method of the particles.

Reply: In response to this comment, we have added several sentences regarding the size and collection methods of our samples in the revised manuscript. Moreover, we have updated Tables S3-S4 to include particle size information for power plant coal fly ash and steelwork fly ash samples. Please find additional details below.

1) For desert dust samples, we have added the following sentence in the revised manuscript (page 5): "Desert dust samples used in this work were collected from topsoil in corresponding regions, and the volume-equivalent diameters were in the range of 1.1-87.2 μm (Tang et al., 2019; Chen et al., 2020)."

2) For power plant coal fly ash samples, we have added the following sentence in the revised manuscript (page 6): "These samples were obtained from baghouse rows or electrostatic precipitators in coal power plants (Li et al., 2026), and their volume equivalent diameters were in the range of 16.9-67.6 μm (Table S3)."

3) For steelwork fly ash samples, we described sample collection in our original manuscript; in the revised manuscript (page 6) we have added one sentence to describe their size: "…and their volume-equivalent diameters were in the range of 4.6 to 176.4 μm (Table S4)."

4) For biomass burning aerosol, TSP samples were collected for biofuel burning. In the revised manuscript (page 7), we have added one sentence for further clarification: "Since no size selection was applied, the samples represent total suspended particles (TSP) from biofuel burning."

5) For municipal waste fly ash, oil bottom ash, and urban particulate matter, we have added one sentence in the revised manuscript (page 8) to provide their size information: "Their volume-equivalent diameters were 115.9, 21.2, 15.4 and 5.9 μm, respectively."

l.433: The earlier study does not contradict the mechanisms of isotopic fractionation during the evaporation-condensation process in combustion. Industrial particles (< 50 μm) were collected prior to emission, so that the actual aerosols emitted into the ambient atmosphere can be smaller particles with lighter δ56Fe. The aerosol particles collected on impaction plates can include mineral dust aerosols, so that the average δ56Fe of total Fe is similar to that for desert dust Fe. Please provide more precise information and reconsider the interpretation.

Reply: We agree that ambient aerosol particles Flament et al. (2008) may contain mineral dust. However, as Flament et al. (2008) collected ambient aerosol particles at a site which is only ~5 km from a large steelwork plant, one would expect the ambient aerosol Fe to carry isotopic signature of aerosol Fe from steelwork. In response to this comment, we have made the following changes in the revised manuscript:

1) The first sentence of this paragraph (page 21) has been changed to "It is noted that an earlier study (Flament et al., 2008) did not fully support what was proposed by Kurisu et al. (2016b)."

2) Moreover, we have added two sentences in this paragraph (page 21) to further interpret the work by Flament et al. (2008): "Ambient aerosol particles Flament et al. (2008) investigated may also contain dust particles, and thus the δ^{56}Fe values they reported for ambient aerosols

may not fully represent those for aerosol particles emitted by steelwork. On the other hand, if aerosol Fe emitted by steelwork was significantly lighter than dust Fe, one would expect ambient aerosol particles Flament et al. (2008) collected at a site close to a major steelwork plant to exhibit δ^{56}Fe values lower than +0.1‰."

Technical comments

l.238: Please correct this to Figure 2.

Reply: We would like to thank ref #2 for pointing out this typo, and we have corrected it in the revised manuscript (page 11).