Measurement report: Stoichiometry of dissolved iron and aluminum as an indicator of the factors controlling the fractional solubility of aerosol iron: Results of the annual observations of size-fractionated aerosol particles in Japan

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Abstract.

~~Atmospheric deposition of iron (Fe) in aerosol particles is enhanced primary production on the ocean surface, resulting in promoting the uptake of carbon dioxide into the surface seawater. Atmospheric~~The atmospheric deposition of iron (Fe) promotes primary production in the surface ocean, ~~resulting~~which results in the enhanced uptake of carbon dioxide into surface seawater. ~~Since~~Given that microorganisms in seawater utilize dissolved Fe (d-Fe) as a nutrient, the bioavailability of Fe in aerosol particles depends on its solubility. However, the factors controlling fractional Fe solubility (Fe_{sol}%) in aerosol particles have not been fully understood. This study performed annual observations of ~~Fe_{sol}%~~the total and dissolved metal concentrations in size-fractionated (seven fractions) aerosol particles at Higashi-Hiroshima, Japan. ~~In particular, the~~The feasibility of the molar concentration ratio of d-Fe relative to dissolved Al ([d-Fe]/[d-Al]) as an indicator of ~~the~~ sources of d-Fe in aerosol particles was investigated because this ratio is likely dependent on the emission sources of Fe (e.g., mineral dust, fly ash, and anthropogenic Fe oxides) and their dissolution processes (proton-~~promoted~~ and ligand-promoted dissolutions). Approximately 70 % of the total Fe ~~and dissolved Fe was~~in total suspended particulate (TSP) were present in coarse ~~and fine~~ aerosol particles, ~~respectively, and the~~whereas about 70% of d-Fe in TSP were mainly found in fine aerosol particles. The average Fe_{sol}% in fine aerosol particles (11.4 ± ~~6.97~~7.0 %) was higher than that of coarse aerosol particles (2.19 ± 2.27-%). In addition, the average ratio of [d-Fe]/[d-Al] in coarse aerosol particles (0.408 ± 0.168) was lower than that in fine aerosol particles (1.15 ± 0.~~803~~80). The range of [d-Fe]/[d-Al] ratios in the coarse aerosol particles (0.121–0.927) was similar to that obtained by proton-promoted ~~dissolutions~~dissolution of mineral dust (0.1–1.0), ~~indicating~~which indicates that the d-Fe in coarse aerosol particles ~~were~~was derived from mineral dust. The [d-Fe]/[d-Al] ratios of fine aerosol particles ranged from 0.386 to 4.67, and [d-Fe]/[d-Al] ratios greater than 1.~~5~~50 cannot be explained by proton-~~promoted dissolution~~ and ligand-promoted ~~dissolution~~dissolutions (1.~~0~~00 < [d-Fe]/[d-Al] < 1.~~5~~50). The [d-Fe]/[d-Al] ratio correlated with the enrichment factor of Fe in fine aerosol particles (r: 0.505), ~~indicating~~which indicates that anthropogenic Fe with a high [d-Fe]/[d-Al] ratio was the source of d-Fe in fine aerosol particles. The high [d-Fe]/[d-Al] ratio was attributed to anthropogenic Fe~~-~~ oxides emitted from high-temperature combustions~~ (high-temp FeOx).~~. Finally, the fraction of ~~high-temp FeOx~~anthropogenic Fe oxides to d-Fe in total suspended particulate (TSP) was calculated based on the [d-Fe]/[d-Al] ratio of aerosols and their emission source samples. As a result, the fraction of ~~high-temp FeOx~~anthropogenic Fe oxides to d-Fe in TSP varied from 1.48 % to 80.7 %. ~~The~~A high fraction was ~~found~~observed in summer when air masses originated from industrial regions in Japan. By contrast, approximately 10 % of d-Fe in the TSP samples collected in spring and during Asian dust events was derived from ~~high-temp FeOx,~~anthropogenic Fe oxides when air masses ~~were~~ frequently transported from East Asia to the Pacific Ocean. Thus, mineral dust ~~is~~was the dominant source of d-Fe in Asian outflow to the Pacific Ocean.

1. Introduction

Primary production in high-nutrient~~,~~ low-chlorophyll regions, such as the North Pacific, Eastern Equatorial Pacific, and Southern Ocean, is limited by the depletion of dissolved Fe (d-Fe, Martin and Fitzwater, 1988; Boyd et al., 2007; Moore et al., 2013; Tagliabue et al., 2017). The atmospheric deposition of Fe activates primary productions in surface seawater, ~~enhancing~~which enhances the oceanic uptake of atmospheric CO_2 (Martin, 1990; Martin et al., 1994; Falkowski et al., 2000; Jickells et al., 2005). In the last glacial–interglacial period, the atmospheric CO_2 concentration was inversely correlated with the supply of mineral dust to the Southern Ocean (Martínez-Garcia et al., 2009, 2011, 2014). Thus, the fertilization of d-Fe in surface seawater via aerosol deposition is an important driver of the global climate system. Given that phytoplankton in surface seawater utilizes d-Fe as ~~nutrients~~nutrient, the bioavailability of Fe in aerosol particles depends on ~~their~~its solubility (Moore et al., 2013). Iron in aerosols ~~is not highly~~has low solubility in water ~~soluble~~, and the solubility of fractional Fe ~~solubility~~ (Fe_{sol}% = ~~[dissolved~~ (d-Fe/total Fe~~]~~) × 100) in marine aerosols ranges from 0.1 % to 90 % (Sholkovitz et al., 2012; Mahowald et al., 2018). ~~Differences in~~Factors controlling Fe_{sol}% include the differences in the Fe_{sol}% among emission sources (e.g., mineral dust ~~vs.~~versus anthropogenic aerosol) and ~~the~~ atmospheric processes of Fe-bearing particles ~~are factors controlling Fe_{sol}%~~ (Sedwick et al., 2007; Sholkovitz et al., 2009; Mahowald et al., 2018; Ito et al., 2019, 2021). ~~In fact,~~In addition, previous studies revealed that the factors have size dependences because fine aerosol particles ~~have been found to~~ yield higher Fe_{sol}% than coarse aerosol particles derived from either or both anthropogenic Fe and atmospheric processes~~, as a result of size-fractionated samplings of marine aerosols~~ (Buck et al., 2010a; Chance et al., 2015; Sakata et al., 2018; Kurisu et al., 2021; Baker and Jickells, 2006, 2017; Baker et al., 2020; Gao et al., 2019). However, the factors controlling Fe_{sol}% in aerosol particles have not been fully understood.

~~The source~~Source apportionment of ~~dissolved~~ d-Fe in aerosol particles has been conducted based on ~~the basis of~~ the correlation analysis of Fe_{sol}% with the concentrations and enrichment factors (EFs) of coexisting elements. ~~For example, the~~The EFs of vanadium (V) and lead (Pb) are used as tracer elements of heavy-oil and coal combustion processes, respectively (Sholkovitz et al., 2009; Conway et al., 2019; Hsieh et al., 2022). ~~Indeed, the~~The correlations of Fe_{sol}% with the EFs of V and Pb are useful for evaluating the presence of anthropogenic Fe. However, quantitative ~~evaluating~~evaluation of the fraction of anthropogenic Fe in d-Fe in aerosol particles is difficult. Therefore, an indicator that can estimate the fraction of anthropogenic Fe in d-Fe in aerosols is required to evaluate quantitatively the Fe supply from aerosols to the ocean surface. The fraction of anthropogenic Fe ~~has~~was recently ~~been~~ estimated ~~by~~ using the Fe isotope ratio ($\delta^{56}Fe$~~) because~~); anthropogenic Fe has a lower $\delta^{56}Fe$ than mineral dust (Kurisu et al., 2016a and b, 2019, 2021; Conway et al., 2019). Although the $\delta^{56}Fe$ of total Fe in marine aerosol particles has been reported by previous studies, data on the $\delta^{56}Fe$ of d-Fe in marine aerosol particles are limited due to analytical difficulties, including high filter blanks (Conway et al., 2019; Kurisu et al., 2021). ~~Considering~~Given that the ~~fractions~~fraction of anthropogenic Fe in d-Fe depends on the Fe_{sol}% of anthropogenic Fe and mineral dust, the contribution of ~~non-crustal~~anthropogenic Fe ~~in~~to the total Fe is not always directly reflected ~~in~~to that of d-Fe. Therefore, attaining the

~~ability~~capability to produce indicators for ~~the~~ source estimation of d-Fe in aerosol particles with low analytical difficulty is ideal.

The stoichiometry of the mineral dissolution of major elements (e.g., Si, Al, Fe, and Mg) has been investigated to understand the dissolution processes of minerals in the environment (Acker and Bricker, 1992; Brantley et al., 2008; Bibi et al., 2011; Bray et al., 2015). The stoichiometry of mineral dissolution is controlled by acid type, pH, and ionic strength~~, as well as~~ and the presence or absence of organic ligands (Brantley et al., 2008; Bray et al., 2015). Therefore, the ratios of dissolved concentrations of major elements vary depending on their dissolution processes from ~~the~~ minerals (Acker and Bricker, 1992; Brantley et al., 2008; Bibi et al., 2011; Bray et al., 2015). However, studies on Fe dissolution from aerosols have focused exclusively on Fe and ~~have paid little attention to~~neglected other dissolved metals in aerosol particles. In general, although the stoichiometry of mineral dissolution is discussed based on the ratio of the dissolution rate of major elements versus that of Si (Acker and Bricker, 1992; Brantley et al., 2008; Bibi et al., 2011; Bray et al., 2015), the data on total and dissolved Si concentrations in aerosol particles are limited relative to those on Fe and Al concentrations (Jickells et al., 2016). ~~Discussing~~Discussion of the dissolution processes of mineral dust ~~by~~ using Mg ~~concentrations~~concentration is difficult because Mg in marine aerosol particles is usually derived from sea spray aerosol ~~(SSA).~~. Therefore, this study focused on the molar ratio of d-Fe to dissolved ~~Fe to~~ Al ([d-Fe]/[d-Al]) ~~in aerosol particles~~ as ~~the~~an indicator of the sources of d-Fe in aerosol particles because (i) previous studies have frequently determined d-Fe and d-Al concentrations in aerosol particles, and (ii) mineral dust is the dominant source of Fe and Al.

Iron-bearing particles derived from mineral dust and anthropogenic Fe have different chemical compositions and mineralogy. Mineral dust is mainly composed of crystalline aluminosilicates (Jeong and Achterberg, 2014; Jeong et al., 2014; Jeong, 2020). ~~Fly~~The fly ash emitted from anthropogenic high-temperature combustion processes can be categorized into two groups: non-magnetic and magnetic particles. Non-magnetic particles in fly ash consist of aluminosilicate glass (Furuya et al., 1987; Rivera et al., 2015). ~~The dominant Fe species in this~~This fraction is dominated by poorly ordered polymerized hydroxyl Fe(III) (Rivera et al., 2015). The magnetic fraction is composed of crystalline Fe oxides (e.g., hematite and magnetite) formed through the condensation of evaporated Fe during gas cooling (Kukier et al., 2003; Fomenko et al., 2019; Czech, 2022). ~~Both particle types~~ Magnetic and non-magnetic particles have been found in ambient aerosol particles (Li et al., ~~2017~~2021; Zhu, Y. et al., 2020, 2022~~) and have higher Fe_{sol}% than mineral dust (Kurisu et al., 2016a, 2019).~~). Therefore, ~~the~~ differences in the mineralogy and chemical composition ~~between~~of mineral dust, ~~non-magnetic, and~~ magnetic, and non-magnetic particles ~~likely~~possibly affect the [d-Fe]/[d-Al] ratio in aerosol particles. ~~For example, the~~The [d-Fe]/[d-Al] ratio of clay minerals ranges from 0.100 to 1.00 (Kodama and Schnitzer, 1973; Lowson et al., 2005; Bibi et al., 2011; Bray et al., 2015), whereas that of fly ash emitted from coal and municipal solid-~~-~~waste incinerators (MSWIs) is less than 0.~~1~~100 (Seidel and Zimmels, 1998; Kim et al., 2003; Huang et al., 2007). In addition, the [d-Fe]/[d-Al] ratio of ~~the~~ aggregates of Fe oxide nanoparticles derived from anthropogenic emissions is expected to be higher than that of mineral dust and fly ash because Fe oxide nanoparticles ~~have~~contain minimal amounts of coexisting elements (Kukier et al., 2003; Fomenko et al., 2019). ~~The~~If the [d-Fe]/[d-Al] ratio of mineral dust and anthropogenic Fe is generalized, the fractions of mineral dust and anthropogenic Fe in d-Fe in aerosol

particles can be estimated based on the ~~basis of the~~ [d-Fe]/[d-Al] ratio ~~if the [d-Fe]/[d-Al] ratio of mineral dust and anthropogenic Fe is generalized.~~ .

In 2013, the annual observation of Fe, Al, and other trace ~~metals~~metal concentrations and their fractional solubilities in size-fractionated aerosol particles (seven fractions) was conducted in Higashi-Hiroshima, Hiroshima, Japan~~. Our previous study identified that fine aerosol particles collected~~ (Fig. 1). Air masses at the sampling site ~~contained~~ in summer were mainly derived from the domestic region of Japan, whereas air masses passing over East Asia arrived at the site in winter and spring (Fig. S1). Our sample set included samples affected by Asian dust and serious haze events associated with anthropogenic ~~Fe with a negative δ^{56}Fe (Kurisu et al. 2016a). Therefore, the sampling site is useful~~emissions, which allowed us to obtain aerosol samples with considerable differences depending on the size dependence and seasonal variation expected for ~~evaluating the availability of the [~~Fe chemistry and d-Fe~~]/[d-Al] ratio as an indicator of the fractions of mineral dust and anthropogenic Fe in d-Fe in aerosol particles. In addition, the ground~~ sources. Ground-based long-term observations of Fe_{sol}% are important ~~for complementing~~to complement the observed data on Fe_{sol}% in marine aerosols because (i) mineral dust and anthropogenic Fe (excluding ship emissions) are emitted in continental regions, and (ii) the representativeness of ~~the~~ Fe_{sol}% data obtained by ship-board observation is often problematic due to ~~the~~ difficulties in the long-term observation of marine aerosol particles at fixed stations (Mahowald et al., 2018). ~~The ground-based observation of Fe_{sol}% in aerosol particles is a strategy for obtaining long-term data on Fe_{sol}% because mineral dust and anthropogenic Fe (excluding ship emissions) are emitted in continental regions. In addition, Fe-bearing particles~~In addition, mineral dust and anthropogenic Fe internally mixed with sulfate, nitrate, and organics are frequently found in the continental atmosphere, ~~indicating~~which indicates that ~~the~~ chemical aging of Fe-bearing particles begins during transport in continental regions. ~~In the chemical aging of Fe-bearing particles during transport from East Asia to the Pacific Ocean,~~Previous studies reported that atmospheric processing after passing over Japan has a small effect on the Fe_{sol}% of marine aerosol particles in the case of Fe-bearing particles during their transport from East Asia to the Pacific Ocean (Buck et al., 2013; Sakata et al., 2022). ~~Given that~~ Japan is located at the rim of East Asia (or the entrance of the North Pacific Ocean), and thus, it can ~~collect~~accumulate mineral dust and anthropogenic Fe aged during their transport from East Asia to Japan. Therefore, ~~it~~Japan can be an important observation site for the characterization of aerosols transported to ~~the~~ North Pacific Ocean. This study ~~aims~~aimed to evaluate the availability of ~~the~~ source identification of d-Fe in aerosol particles based on [d-Fe]/[d-Al] ratios and ~~to understand~~gain insights into the seasonal variability of the ~~fraction~~fractions of mineral dust and anthropogenic Fe in d-Fe in aerosols.

2. Method

2.1. Aerosol sampling

Aerosol sampling was performed at Higashi-Hiroshima, Hiroshima, Japan (Fig. 1~~,~~; 34.40°N, 132.71°E). Size-fractionated aerosol particles were collected ~~by~~ using a high-volume air sampler (MODEL 123-SL, Kimoto, Japan) with a ~~sierra~~Sierra-type

cascade impactor (TE-236, Tisch Environmental Inc., USA) installed on a roof 10 m above ground level. The cascade impactor had seven stages, and the aerodynamic diameters of the aerosol particles collected in each stage from ~~stages~~Stage 1 to Stage 7 followed the order ~~of~~ >10.2, 4.2–10.2, 2.1–4.2, 1.3–2.1, 0.69–1.3, 0.39–0.69, and <0.39 μm. ~~Coarse~~The coarse aerosol particles were coarser than 1.3 μm (~~stages~~Stages 1~~ to ~~4), whereas the fine aerosol particles were finer than 1.3 μm (~~stages~~Stages 5~~ to ~~7). Aerosol particles were collected onto cellulose filters (~~stages~~Stages 1~~ to ~~6: TE-230WH, Tisch Environmental Inc., USA, and ~~S~~ Stage 7: Whatman 41, 8 × 10 ~~inches~~in^2, GE Healthcare, USA). Aerosol samplings during non-dust events were conducted every month from December 2012 to December 2013 (Table S1). The flow rate of the air sampler was fixed at 0.566 m^3~~/~~ min^{-1}. The typical sampling period was 2 weeks. However, if the sampling flow rate decreased due to ~~the~~ clogging of the ~~stage~~ Stage 7 filter, aerosol sampling was immediately stopped. Aerosol samplings were also performed during two dust events associated with haze and Asian dust ~~in~~on January 31, 2013 to February 1, 2013 and on March 4, 2013 to March 9, 2013, respectively. Aerosol mass concentrations in China exceeded 600 μg m^{-3} at the end of January 2013 (Tian et al., 2014; Wang et al., 2014), and their transported particles can be collected during the haze event. The sampling periods for the ~~polluted~~haze and Asian dust events were 1 and 5 days, respectively~~, and~~. The sampling periods for haze and Asian dust events were decided based on ~~the basis of~~ a chemical weather forecasting system, which predicted the mass concentrations of Asian dust and sulfate aerosols (Uno et al., 2004). ~~Serious haze events occurred in East Asia at the end of January when aerosol mass concentrations exceeded 600 μg/m^3 (Tian et al., 2014; Wang et al., 2014). Therefore, the haze sample was influenced by the serious air pollution event in East Asia. The backward~~Backward trajectories at the altitude of 100 m were calculated ~~by~~ using the Hybrid Single-Particle Lagrangian-Integrated Trajectory model (Stein et al., 2015). Global Data Assimilation System (GDAS 0.5 degree archive) was used to collect ~~the meteorology~~meteorological data. The total run time was 72 h, and the backward trajectory was calculated every 6 h. Figs. ~~Backward~~ S1 and S2 show the backward trajectories for non-dust and dust events ~~are shown in Figs.~~ S1 and S2, respectively.

2.2. Major ion concentrations

Aerosol particles on approximately one-fourth of the filter strips were used for the extraction of major ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}) ~~by~~ using 5 mL ~~of~~ ultrapure water (MQ, Merck Millipore, USA) in polypropylene vials with ultrasonication for 30 min. Suspended particles in the extract were removed ~~by~~ using a hydrophilic polytetrafluoroethylene (PTFE) filter (ϕ: 0.20 μm, DISMIC, ADVANTEC, Tokyo Roshi Kaisha, Ltd., Japan). All materials used for the extraction of major ions were rinsed thrice with ~~MQ~~ultrapure water ~~three times~~ before use.

Major ion concentrations were determined through ion chromatography (ICS–1100, Dionex Japan, Japan). The guard columns for cations and anions were Dionex Ion Pack CG12A and AG22, respectively. The separation columns for cations and anions were Dionex CS12A and AS22, respectively. The eluents for cations and anions were methanesulfonic acids and ~~the~~a mixed solution of 4.5 mmol~~/~~ L^{-1} Na_2CO_3 and 1.4 mmol~~/~~ L^{-1} $NaHCO_3$, respectively. The ~~detail~~detailed procedure of ion chromatography was described ~~by~~in the work of Sakata et al. (2014).

Non-sea-salt (nss) K^+, Mg^{2+}, Ca^{2+}, and SO_4^{2-} concentrations were estimated as follows:

$$[\text{nss-X}]_{\text{aerosol}} = [\text{Total-X}]_{\text{aerosol}} - [\text{Na}]_{\text{aerosol}} \times ([\text{X}]/[\text{Na}^+])_{\text{seawater}}, \text{ (Eq. 1)}$$

where X is the molar concentration of either K^+, Mg^{2+}, Ca^{2+}, or SO_4^{2-}. ~~All the quantitative data of the major ions in size-fractionated aerosol particles are shown in Table S2.~~The molar ratios of $[K^+]/[Na^+]$, $[Mg^{2+}]/[Na^+]$, $[Ca^{2+}]/[Na^+]$, and $[SO_4^{2-}]/[Na^+]$ were 0.0213, 0.113, 0.0213, and 0.0596, respectively (Nozaki, 2001).

2.3. Estimation of aerosol pH

The aerosol pH of fine aerosol particles was estimated ~~by~~ using the thermodynamic ~~model~~ E-AIM Model IV (Clegg et al., 1998; Friese and Ebel, 2010). The calculation parameters for the model were ~~temperature, relative humidity,~~ $[H^+]$, $[NH_4^+]$, $[Na^+]$, $[Cl^-]$, $[NO_3^-]$, ~~and~~ $[SO_4^{2-}]$~~.~~], temperature, and relative humidity (RH). Ammonia gas concentration was not measured during the sampling campaign. Therefore, aerosol pH was calculated through a reverse mode that tended to overestimate aerosol acidity (Song and Osada, 2020). Previous studies have reported that nonvolatile cations (e.g., Mg^{2+} and Ca^{2+}) affect the calculation results of aerosol pH (Guo et al., 2018; Pye et al., 2020). $[Na^+]$ was used as a representative of nonvolatile cations (= $[Na^+] + [K^+] + 2 \times [Mg^{2+}] + 2 \times [Ca^{2+}]$) to estimate aerosol pH because the E-AIM model IV cannot incorporate the concentrations of nonvolatile cations other than Na^+ (Tao and Murphy, 2019a). The $[H^+]$ concentration in aerosol particles was estimated on the basis of ~~the~~ charge balance. Several samples had negative $[H^+]$ concentrations and were thus excluded from the estimation of aerosol pH. ~~Aerosol pH was calculated by~~In addition, E-AIM model IV cannot calculate aerosol pH when the RH is below 60 %. The average RH during each sampling period was higher than 60 %, except for those of aerosol samples collected in April and May 2013. The aerosol pH collected in April and May was calculated under the assumption of 60 % RH because the average RHs of the samples for these months were 59.4 % and 59.5 %, respectively. Aerosol pH was calculated using the following equation:

$$\text{Aerosol pH} = -\log_{10}(m_{H+} \times \gamma_{H+}), \text{ (Eq. 2)}$$

where m_{H+} and γ_{H+} are the molar fraction and activity coefficient of H^+, respectively.

2.4. Trace metal concentrations

~~The target trace metals in this study were Al, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sb, and Pb.~~ Approximately one-fourth of the filter strips ~~was~~were used for acid digestion to determine the total trace metal concentrations. Each filter piece was digested with a mixed acid solution of 15.2 mol~~/~~ L^{-1} HNO_3, 9.3 mol~~/~~ L^{-1} HCl, and 20 mol~~/~~ L^{-1} HF in a 7 mL ~~of~~ perfluoroalkoxyalkane vial heated at 120 °C for 12 h (all mineral acids were procured from TAMAPURE AA-100, Tama Chemicals Co., Ltd., Japan). Subsequently, the mixed acid was evaporated to dryness. The dried residue was dissolved in 5 mL ~~of~~ 0.15 mol~~/~~ L^{-1} HNO_3 heated at 120 °C for 3 h. The solution was filtered through a hydrophilic PTFE filter (ϕ: 0.20 µm, Dismic®, 25HP020AN, Advantec, Japan) to prepare the analytical solution. Soluble metals in aerosol particles were extracted ~~by~~ using 5 mL ~~of MQ~~ultrapure water with ultrasonication for 30 min. Then, the extracted solution was filtrated with a

hydrophilic syringe PTFE filter. The filtrated solution was acidified to prepare a 0.15 mol~~/~~ L^{-1} HNO_3 solution by ~~adding~~the addition of 15.3 mol~~/~~ L^{-1} HNO_3. The filtrated solutions for total and dissolved metal concentration analyses were diluted with 0.15 mol~~/~~ L^{-1} HNO_3 by factors of 10–1000.

The total and dissolved metal concentrations of the sample solution were determined via inductively coupled plasma mass spectrometry (ICP–MS, Agilent 7700, Agilent, Japan). The sample introduction system consisted of a borosilicate nebulizer (MicroMist, Agilent, Japan) and a quartz Scott double-pass spray chamber. The elements in the sample solution were ionized by ~~an~~ argon plasma (RF power: 1500 W, Ar flow for ~~plasma~~career gas: 1.0 L~~/~~ min^{-1}). The ions were introduced into the detection system by passing them through ~~Ni~~nickel sampling and skimmer corns. The ion beam was focused ~~by using~~with x-type ion lenses. ~~The He~~Helium collision mode was ~~employed~~used to reduce interference from oxides (e.g., $^{40}Ar^{16}O+$ for ^{56}Fe). Helium gas was injected into a dynamic reaction cell at a rate of 3.6 mL~~/~~ min^{-1}. Then, mass selection was performed ~~by using~~on a quadrupole system. Target metal concentrations were measured in pulse (ion-counting) mode. The sensitivity drift during ~~the~~ measurements was corrected ~~by~~ using the internal standard of 1 ng~~/~~ g ~~of In. All quantitative data on total and dissolved Fe and Al concentrations and their fractional solubilities are shown in Table S3. The total and dissolved metal concentrations of other target elements are shown in Tables S4 and S5, respectively.~~$^{-1}$ indium.

2.5. Estimation of EF of Fe and Fe_{sol}%

The total and dissolved metal concentrations in TSP were calculated by the summation of the target metal concentrations in all sampling stages. Crustal and non-crustal Fe concentrations and the EF of target metals normalized by the average continental crust were calculated by using the following equations:

$$\text{Crustal Fe} = Al_{crust} \times (Fe/Al)_{aerosol}, \text{ (Eq. 3)}$$

$$\text{Non-crustal Fe} = \text{Total Fe} - \text{crustal Fe}, \text{ (Eq. 4)}$$

$$EF = (M/Al)_{aerosol}/(M/Al)_{crust}, \text{ (Eq. 5)}$$

where M is the target metal. Iron and Al concentrations in the average continental crust (Fe/Al: 0.684) were acquired by referring to Taylor (1964). Given the variability of the Fe/Al ratio in crustal materials, significant enrichment of the Fe derived from anthropogenic emissions is usually recognized at EF values higher than 10.0. The EF equation suggests that about 90 % of Fe is derived from anthropogenic sources when the EF is 10.0. Given that the emission amount of crustal Fe is an order of magnitude higher than that of anthropogenic Fe, the EF for Fe in aerosol particles is usually below 10.0, except for aerosol samples collected near steel plants and in urban areas. Therefore, classification of Fe as anthropogenic Fe by the criterion EF > 10.0 substantially simplifies the origin of Fe in aerosol particles. If the variation of Fe/Al ratio in natural-source aerosol is limited in a narrow range, aerosols with EF > 2.00 can still be evaluated as aerosol samples containing anthropogenic Fe component to a certain degree. The small variability of the Fe/Al ratio in desert soil in East Asia was confirmed (average ± 1σ standard deviation (ave.±1σ): 0.555 ± 0.170, range: 0.294–1.05, Nishikawa et al., 2013; Ding et al., 2001; Cao et al., 2008; Liu, X. et al., ~~Their concentrations in the average continental crust were acquired by referring to Taylor (1964). The fractional solubility of target metals~~2022 and references therein). The Fe/Al ratio in mineral dust exhibits a small variability, and thus,

enrichment of anthropogenic Fe is recognized when the EF of Fe is higher than 2.00 (Fe/Al > 1.37). The Fe_{sol}% in aerosol samples was calculated by using the following equation:

Fractional solubility (%) = (~~Dissolved M~~d-Fe/total M) × 100. (Eq. 6)

3. Results and Discussion

~~3.1. Major ion concentrations~~

~~3.1.1. Cations~~

~~Sodium ion, Mg^{2+}, and Ca^{2+} were mainly distributed in coarse aerosol particles, accounting for 88.3 %, 84.8 %, and 79.3 % of the ions in TSP, respectively (Figs. 2a–2c). Sodium ion in aerosol particles was mainly associated with sea spray aerosol (SSA). Magnesium ion was mainly derived from SSA considering that nss Mg^{2+} accounted for 26.2 ± 22.4 % of the total Mg^{2+}. By contrast, almost all Ca^{2+} (90.8 ± 9.45 %) was present in the form of nss Ca^{2+}. Calcium ion concentration was higher in spring (March to May) than in other seasons and during Asian dust events (Fig. 2b). A large amount of Asian dust is transported from the Gobi or Taklamakan Deserts in spring (Uematsu et al., 1983; Sullivan et al., 2007a). Therefore, the high Ca^{2+} concentration in spring was attributed to Asian dust. Potassium ion and NH_4^+ were mainly distributed in fine aerosol particles, which accounted for 68.2 ± 9.69 % and 83.0 ± 3.49 % of the ions in TSP, respectively (Figs. 2d and 2e). More than 90 % of K^+ in fine aerosol particles (annual average: 94.5 ± 14.8 %) was present in the form of nss K^+. The nss K^+ in fine aerosol particles is mainly derived from either biomass burning or coal combustion (Echalar et al., 1995; Simoneit et al., 2002; Yu et al., 2018). The discussion on the size and seasonal variation of NH_4^+ with NO_3^- and SO_4^{2-} is provided in the next section.~~

~~3.1.2. Anions~~

~~Chloride ion dominated in coarse aerosol particles, which contributed 79.5 ± 14.1 % of Cl^- in TSP (Fig. 2f). SSA is the dominant source of Cl^- in aerosol particles. However, the Cl^-/Na^+ mass ratio of aerosol particles was not identical to that of seawater (Fig. S3a). Chloride ion concentration in coarse aerosol particles was depleted relative to the expected Cl^- concentration in non-aged SSA (= $Na^+_{aerosol} \times [Cl^-/Na^+]_{seawater}$), and the depletion ratio of Cl^- in coarse aerosol particles to Cl^- in non-aged SSA was 34.7% ± 28.2%. Cl^- depletion was caused by the chemical reaction of NaCl with HNO_3 and H_2SO_4 as follows (Finlayson-Pitts, 2003):~~

~~$NaCl + HNO_3 \longrightarrow NaNO_3 + HCl(g)$, (R1)~~

~~$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl(g)$. (R2)~~

~~The frequent enrichment of Cl^- in fine aerosol particles relative to that in non-aged SSA (Fig. S3a) and in contrast to that in coarse aerosol particles indicated that emission sources other than SSA contributed to Cl^- in fine aerosol particles. Cl^- enrichment was observed in aerosol samples collected in winter and spring when air masses mainly originated from East Asia (Fig. S1 and S3a). Previous studies have reported that anthropogenic emissions (e.g., coal combustion, industrial processes,~~

~~and MSWI) and biomass burning are the dominant sources of HCl and Cl^- in fine aerosol particles in East Asia (Fu et al., 2018; Liu et al., 2018). Indeed, the correlation of excess Cl^- concentration (= −1 × Cl^- loss) with nss K^+ is a tracer of biomass burning and coal combustion (r: 0.570). In addition, pre-existing particles, including $CaCO_3$ in mineral dust, act as the sink of Cl species (Sullivan et al., 2007b; Tobo et al., 2010). Therefore, the enrichment of Cl^- in fine aerosol particles was caused by the uptake of anthropogenic Cl^- by pre-existing particles.~~

~~Sulfate ions and NH_4^+ were mainly distributed in fine aerosol particles (Figs. 2e and 2g) and accounted for 75.8 ± 11.1 % and 88.8 ± 7.68 % of the total anions and cations in fine aerosol particles, respectively. The average fraction of nss SO_4^{2-} to total SO_4^{2-} (nss-SO_4^{2-}/total SO_4^{2-}) in coarse and fine aerosol particles were 70.1 ± 23.1 % and 99.3 ± 1.44 %, respectively. Thus, nss SO_4^{2-} was dominant in coarse and fine aerosol particles. Ammonium ion concentration had a good correlation with but was higher than nss SO_4^{2-} concentration (Fig. S3b). This result indicated that ammonium salts other than $(NH_4)_2SO_4$ and NH_4HSO_4 were present in fine aerosol particles. Ammonium ion concentration was found to have an excellent correlation with 2 × [nss SO_4^{2-}] + [NO_3^-] in fine aerosol particles (Fig. S3c). The slope of the regression line was 0.965, indicating that $(NH_4)_2SO_4$ and NH_4NO_3 were the dominant major ion components in fine aerosol particles.~~

~~Nitrate ion had concentration peaks not only in fine aerosol particles but also in coarse aerosol particles (Fig. 2h). The average fractions of NO_3^- in coarse and fine aerosol particles in TSP were 61.3 ± 12.3 % and 36.9 ± 10.5 %, respectively. As previously mentioned, NO_3^- in coarse aerosol particles was derived from Cl^- depletion as described in R1. Assuming that NO_3^- caused the depletion of all Cl from SSA in coarse aerosol particles, SSA associated NO_3^- accounted for only 35.1 ± 25.1 % of NO_3^- in coarse aerosol particles. Therefore, NO_3^- ions were mainly present in coarse aerosol particles other than SSA (non-SSA NO_3^-). Previous studies have reported that mineral dust is the dominant driver of NO_3^- concentration in coarse aerosol particles (Karydis et al., 2016, Kakavas et al., 2021). In fact, the good correlation between nss Ca^{2+} and non-SSA NO_3^- (= total NO_3^- − Cl depletion) found in our coarse aerosol particles (Fig. S3d) indicated that non-SSA NO_3^- was present in coarse aerosol particles in the form of $Ca(NO_3)_2$. However, our previous study identified gypsum ($CaSO_4 \cdot 2H_2O$) rather than $Ca(NO_3)_2$ as the dominant secondary Ca species in coarse aerosol particles collected in January, November, and the Asian dust event (Miyamoto et al., 2020). Recent studies have demonstrated that hygroscopic $Ca(NO_3)_2$ on the surfaces of mineral dust reacted with $(NH_4)_2SO_4$, resulting in the formation of NH_4NO_3 and $CaSO_4 \cdot 2H_2O$ (Wu et al., 2019, 2020). Thus, NO_3^- taken up in the reaction with $CaCO_3$ is considered to exist in the form of NH_4NO_3 instead of $Ca(NO_3)_2$.~~

~~3.2.~~3.1. Total Fe and Al concentrations

The total Fe and Al concentrations in the TSP collected during the non-dust event were 256–1561 and 170–1716 ng m^{-3}, respectively (Figs. ~~3a~~2a and ~~3b~~2b). Coarse aerosol particles accounted for 69.4 ± 7.~~19~~2 % and 72.9 ± 7.~~55~~6 % of the total Fe and Al in TSP, respectively. The total Fe and Al concentrations were higher in spring (March to May) and Asian dust events than in other seasons (Figs. 2a and 2b). A higher Ca^{2+} concentration, as a marker of Asian dust, was also observed in spring than in other seasons (Fig. S3b, Supplemental Note). Therefore, the high Fe and Al concentrations in spring were due to the strong influence of Asian dust ~~in spring (Figs. 3a and 3b). The total Fe and Al concentrations in the samples collected during~~

~~the Asian dust event were considerably higher than those in the samples collected during the non-dust event~~ (Figs. ~~3a~~2a and ~~3b~~2b). The average EF of Fe in the TSP samples collected ~~in~~from summer~~,~~ to fall (June to October) was 2.84 ± 0.83 when air masses mainly originated from Japan~~, was higher than~~ (Fig. S6a). By contrast, the average EF of Fe in ~~TSP samples collected in other seasons (~~the TSP derived from East Asia in winter and spring was 1.57 ± 0.35 (Fig. S6a). Thus, the influences of anthropogenic emission on the total Fe in TSP are more significant in the air mass derived from Japan than that from East Asia (Figs. S1, S2, and ~~S4a~~S6a). The total Al concentrations sharply decreased from May to June, whereas the decrease in the total Fe concentrations ~~did~~was not ~~decrease as significantly~~ as ~~the total Al~~significant (Figs. ~~3a~~2a and ~~3b~~2b). This result indicated that the aerosol particles emitted in Japan contained non-crustal Fe. In addition, the total Fe concentration in the haze event was almost the same as that in the Asian dust event~~. However,~~, whereas the total Al concentration in the haze event was lower than that in the Asian dust event. This result demonstrated that during haze events, the total Fe concentrations were significantly ~~higher than total Al concentrations due to the influence of~~enhanced by the non-crustal Fe emitted from anthropogenic emissions.

The average EFs of Fe in coarse and fine aerosol particles were 1.99 ± 0.~~892~~89 and 2.49 ± 1.09, respectively (~~Fig. 3c~~Figs. 2c and S6a). Therefore, non-crustal Fe may be present in coarse and fine aerosol particles. Non-crustal Fe concentration ~~were~~ in coarse aerosol particles correlated with Cu, Zn, ~~Sb,~~ and ~~Pb in road dust (Figs. 4a–d). The~~Sb ($r > 0.500$, Table S2). These elements in coarse aerosol particles are known as ~~the~~ tracer elements of ~~fragments~~fragment vehicle-related materials in road dust (brake dust: Cu and Sb, and tire wear: Zn~~, and road paint: Pb~~) (Adachi and Tainosho, 2004; Wåhlin et al., 2006; Iijima et al., 2007; Gietl et al., 2010; ~~Sakata et al., 2014;~~ Harrison et al., 2021). ~~A~~The correlation coefficient of non-crustal Fe with Cu as a tracer element of brake ~~pad~~pads was the highest among these tracer elements~~. It is known that~~ (r: 0.747, Table S2). Fe is the most dominant ~~metals~~metal in brake rings (up to 50 wt~~%)~~%), and its concentration is about an order of magnitude higher than that of Al in ~~the~~ brake ~~pad~~pads. Therefore, ~~the~~ brake ~~pad~~pads can increase the EF of Fe in aerosol particles. ~~In fact,~~The EF of Fe in road dust (<40 μm) collected from tunnels and roadsides around the sampling site were 3.41 and 6.04, respectively. Therefore, ~~the~~ resuspensions of brake pad fragments in road dust ~~could~~can be considered ~~as~~ non-crustal Fe in coarse aerosol particles. This result is consistent with the finding of a previous model study ~~because~~, which showed that road dust ~~is~~was the dominant source of Cu and non-crustal Fe in PM_{10} in the Chugoku–Shikoku area (the locality around the sampling site) (Kajino et al., 2020).

In fine aerosol particles, non-crustal Fe concentrations were correlated with Zn, Sb, Cd, and Pb ~~(Fig. 5a–c), which were~~ emitted ~~by~~from high-temperature combustions, including coal combustion, MSWI, and steel/iron industrial processes ($r >$ 0.700, Table S3, Pacyna and Pacyna, 2001; Sakata et al., 2000; Sakata et al., 2014; Kajino et al., 2020). These high-temperature combustion processes emit nanoparticles of hematite and magnetite ~~with a small number of coexisting elements~~, which can increase the EF of Fe in fine aerosol particles. ~~Indeed, in this study, the~~The negative δ^{56}Fe associated with hematite derived from high-temperature combustion processes was detected in aerosol samples collected at the same sampling site (Kurisu et al., 2016a). Therefore, the nanoparticles of hematite and magnetite are likely the dominant ~~source~~sources of non-crustal Fe in fine aerosol particles. In addition, in fine aerosol particles, the non-crustal Fe concentration ~~was weakly~~ correlated with V ~~(Fig. 5d), which is~~as a tracer element of heavy-oil combustion (Nriagu and Pacyna, 1988); however, the correlation factor between

non-crustal Fe and V was lower than those of Zn, Sb, Cd, and Pb (r: 0.601, Table S3). A previous model study predicted that V around the sampling site was derived from vessel emissions in the Seto Inland Sea (Kajino et al., 2020), which is located at the southern part of the sampling site (~~Figure~~Fig. 1~~, Kajino et al., 2020~~). Our results also showed that V concentrations in fine aerosol particles were higher from July to September, during which air masses ~~pass~~passed through the Seto Inland Sea ~~(Figs. 1 and S5a),~~ than in other periods~~.~~ (Figs. 1 and S7a). At this ~~time~~point, the concentrations of Zn, Sb, and Pb did not increase (~~Fig. S5b–d~~Figs. S7b–S7d). Therefore, in addition to the high-temperature combustion processes mentioned above, heavy-oil combustion processes around the Seto Inland Sea ~~likely~~ were ~~the~~possible emission sources of the non-crustal Fe in fine aerosol particles collected in summer.

~~3.3.~~3.2. Size~~-~~ distributions of d-Fe and d-Al concentration and their fractional solubility

~~Dissolved Fe and Al~~ The concentrations ~~in~~of d-Fe and Al in the TSP collected during the non-dust event ranged from 11.4 ~~mg~~ng m^{-3} to 65.0 ng m^{-3} and from 8.30 ng m^{-3} to 40.6 ng m^{-3}, respectively (Figs. ~~6a~~3a and ~~6d~~3d). The Fe_{sol}% and Al_{sol}% of the TSP ranged from 2.00 % to 7.73 % and 1.46 % to 7.39 %, respectively (Figs. ~~S4b~~S6b and ~~S4c).~~S6c), which were within the typical range of Fe_{sol}% in the TSP collected from East Asia and north-western Pacific Ocean (Buck et al., 2006, 2013; Takahashi et al., 2013; Sakata et al., 2022). Although approximately 70 % of the total Fe and Al in the TSP were present in coarse aerosol particles, high concentrations of d-Fe and d-Al were found in fine aerosol particles (Figs. ~~6a~~3a and ~~6d~~3d). The average d-Fe and d-Al concentrations of fine aerosol particles were 27.3 ± 17.4 and 14.3 ± 10.9 ng m^{-3}, which accounted for 72.0 ± 8.~~87~~9 % and 53.1 ± 9.~~90 %, respectively. Thus, d-Fe and d-Al concentrations yielded different size distributions from total Fe and Al concentrations. The reason for the enrichment~~9 % of d-Fe and d-Al in ~~fine aerosol particles was higher Fe_{sol}% and Al_{sol}% in fine aerosol particles than coarse aerosol particles. The average Fe_{sol}% in fine aerosol particles (11.4 ± 6.97%) was about five times higher than that of coarse aerosol particles (2.19 ± 2.27 %, Figs. 6b and 6c). In the case of Al, fine aerosol particles (8.82 ± 6.48 %) yielded twice as much Al_{sol}% as coarse aerosol particles (3.25 ± 3.41 %, Figs. 6e and 6f).~~ the TSP, respectively. Enrichment of d-Fe and d-Al in ~~size fractionated~~fine aerosol ~~samples~~particles has been reported not only in the urban atmosphere (Fang et al., 2017; Hsieh et al., 2022; Liu, L. et al., 2022) but also in the marine atmosphere (McDaniel et al., 2019; Baker et al., 2020; Sakata et al., 2022). These previous studies have reported that the higher amounts of d-Fe and d-Al in fine aerosol particles than coarse aerosol particles were caused by either or both (i) contamination of the anthropogenic aerosol with high Fe_{sol}% and Al_{sol}% and (ii) solubilization of Fe and Al in fine aerosol particles by atmospheric processes. ~~It should be noted that~~The average Fe_{sol}% in fine aerosol particles in this study (11.4 ± 7.0 %) was about five times higher than that of coarse aerosol particles (2.19 ± 2.27 %, Figs. 3b and 3c). In the case of Al, fine aerosol particles (8.82 ± 6.48 %) yielded about twice as much as the Al_{sol}% of coarse aerosol particles (3.25 ± 3.41 %, Figs. 3e and 3f). These results indicated that the Fe in fine aerosol particles is more susceptible to dissolution in water by anthropogenic activities and chemical aging than Al. The Fe_{sol}% and Al_{sol}% in coarse aerosol particles were higher than those in desert dust soil (typical Fe_{sol}% and Al_{sol}%: 0.~~1~~100 %). Therefore, the Fe_{sol}% and Al_{sol}% in coarse aerosol particles ~~were~~ increased ~~by~~due to anthropogenic aerosol and/or atmospheric processes, but the effect was not as pronounced as ~~for~~in fine aerosol particles.

~~3.4.~~3.3. Possible factor controlling Fe_{sol}% and Al_{sol}%

~~3.4.1.~~3.3.1. Coarse aerosol particles

Non-crustal Fe in coarse aerosol particles was derived from brake ~~bad~~pads and tire ware debris in road dust~~.~~ as mentioned above. If road dust is the dominant source of d-Fe in coarse aerosol particles, then the d-Fe concentration ~~is correlated~~correlates with non-crustal Fe concentration. However, ~~a~~no correlation was found between non-crustal Fe and d-Fe ~~concentration~~concentrations in coarse aerosol particles ~~was not found~~ (r: 0.352~~), indicating that~~). Thus, road dust was not the source of d-Fe in coarse aerosol particles. This result is consistent with previous studies ~~because~~in which the Fe_{sol}% of ~~debris of~~ brake pads and tire wear ~~is~~debris was lower than 0.01 % (Shupert et al., 2013; Halle et al., 2021).

The Fe_{sol}% and Al_{sol}% of coarse aerosol particles increased with the decrease in aerosol diameter (~~Fig. 6b, 6c, 6e~~Figs. 3b, 3c, 3e, and ~~6f~~3f). Specific surface area is one of the factors controlling Fe_{sol}% and Al_{sol}% in aerosol particles (Baker and Jickells, 2006, 2017; McDaniel et al., 2019), and the chemical reactivity of aerosol particles ~~is increased~~increases with ~~increasing~~the increase specific surface area ~~(= decreasing~~(decrease in aerosol diameter). Previous studies have reported that ~~the~~ chemical aging of coarse aerosol particles by acidic species, including HNO_3 and H_2SO_4~~, were~~ solubilized Fe in aerosol particles (Takahashi et al., 2011; Zhu et al., 2022). The Fe_{sol}% and Al_{sol}% ~~in~~of coarse aerosol particles correlated with ~~nss~~the molar concentration ratios of nns-SO_4^{2-}~~/-~~ relative to the total Al ~~and nss-SO_4^{2-}/~~or total Fe (Fig. ~~7a).~~4a), [nss-SO_4^{2-}]/[total Fe], and [nss-SO_4^{2-}]/[total Al]). This result is consistent with previous findings ~~because~~showing that aluminosilicates in aerosol particles react preferentially with H_2SO_4 (Sullivan et al., ~~2007a~~2007; Fitzgerald et al., 2015). Furthermore, our previous studies showed that ~~a~~the relative abundance of ferrihydrite formed by hydrolysis of Fe in coarse aerosol particles ~~was~~ increased with ~~decreasing~~the decrease in diameter (Takahashi et al., 2011; Sakata et al., ~~2012~~2022). These results ~~indicated~~indicate that atmospheric processes of coarse aerosol particles by H_2SO_4 ~~promote~~promoted the formation of d-Fe via proton-promoted dissolution or hydrolysis of Fe. By contrast, no good correlation ~~was found between~~of Fe_{sol}% and Al_{sol}% ~~and between~~ with [NO_3^-~~/~~]/[total Fe] and [NO_3^-~~/~~]/[total Al] was found because HNO_3 reacts mainly with Ca-rich particles (e.g., $CaCO_3$) in mineral dust~~, as mentioned above~~ (Fig. ~~7b~~4b, Karydis et al., 2016; Kakavas et al., 2021).

~~3.4.2.~~3.3.2. Fine aerosol particles

Unlike the d-Fe in coarse aerosol particles, the d-Fe concentrations in fine aerosol particles correlated with non-crustal Fe concentrations (Fig.~~8a~~ 5a). Good correlations of d-Fe in fine aerosol particles with concentrations of V, Zn, Sb, and Pb as tracer elements for high-temperature combustions were also found (~~Fig. 8b–8e). Among these tracer elements, the~~Figs. 5b–5e). The correlation coefficient between d-Fe and Zn was the largest (Fig. ~~8e). Since Zn~~5c). Zinc in fine aerosol particles ~~at~~from the sampling sites originated from various high-temperature combustions, including ~~MSWI~~those in MSWIs, steel/iron industries, and coal power ~~plant~~plants (Kajino et al., 2020). Therefore, the non-crustal Fe emitted from high-temperature combustion is one of the dominant sources of d-Fe in fine aerosol particles~~, though it is not easy to identify~~ although identification of specific sources of non-crustal d-Fe around the sampling site~~.~~ was difficult. This result is consistent with our

previous ~~studies because~~study, which showed that negative $\delta^{56}Fe$ associated with high-temperature combustions ~~were~~was detected in fine aerosol particles (Kurisu et al., 2016a).

~~It is known that fine aerosol particles usually yield lower aerosol pH compared~~ In addition to ~~coarse aerosol particles~~ the input of non-crustal Fe with high Fe_{sol}% in fine aerosol particles, aerosol acidification resulted in the high Fe_{sol}% and Al_{sol}% in fine aerosol particles (~~Pye~~Fang et al., ~~2020). Therefore, as well as~~2017; Sakata et al., 2022). Along with coarse aerosol particles, ~~atmospheric processes also contribute to solubilizing Fe~~ Fe_{sol}% and Al_{sol}% in fine aerosol particles~~.~~ did not correlate with $[NO_3^-]$/[total Fe] and $[NO_3^-]$/[total Al] due to the preferential reaction of HNO_3 with Ca^{2+} (Fig. 4d). The Fe_{sol}% and Al_{sol}% ~~of~~ correlated with [nss-SO_4^{2-}]/[total Fe] and [nss-SO_4^{2-}]/[total Al], respectively (Fig. 4c). Moreover, these solubilities increased with the decrease in aerosol pH (Fig. 4e), which indicates that acidification of fine aerosol particles by H_2SO_4 plays a significant role in Fe solubilization. These results are reasonable and supported by previous studies reporting that mineral dust and anthropogenic Fe in fine aerosol particles were ~~weakly correlated with nss-SO_4^{2-}/Fe and nss-SO_4^{2-}/Al, respectively, but not with NO_3^-/Fe and NO_3^-/Al (Figs.~~ covered by sulfate, and internal mixing of these~~7e and 7d). In addition, Fe_{sol}% and Al_{sol}% tended to increase with the decrease in aerosol pH (Fig.7e). These results implied that the Fe_{sol}% and Al_{sol}% of fine aerosol particles increased via aerosol acidification, which occurred through the chemical reaction of Fe- and Al-bearing~~ particles with ~~SO_2 and H_2SO_4. The correlation factor between Al_{sol}% and nss-SO_4^{2-}/Al was higher than that between Fe_{sol}% and nss-SO_4^{2-}/Fe (Figs. 7c and 7d). In addition, the correlation factor of the Fe_{sol}% and nss-SO_4^{2-}/Fe~~ sulfate promoted the dissolution of ~~fine aerosol particles was lower than that of coarse aerosol particles (Figs. 7a and 7c). Given that Al in fine aerosol particles was derived from aluminosilicates, Al_{sol}% was mainly controlled by the acidification of mineral dust. These results are reasonable because previous studies have reported that in fine aerosol particles, mineral dust was covered with sulfates~~ Fe (Sullivan et al., ~~2007a~~2007; Fitzgerald et al., 2015; Li et al., 2017, Zhu, Y. et al., 2020, 2022). ~~By contrast~~However, compared with the correlation factor of Fe_{sol}% with [nss-SO_4^{2-}]/[total Fe], coarse aerosol particles yielded a higher correlation factor than fine aerosol particles (Figs. 4a and 4c). Similar results have been reported by previous studies on Fe_{sol}% in China, which indicated the presence of anthropogenic Fe with high Fe_{sol}% as one of the reasons for the low value of the correlation factor (Zhang et al., 2022, 2023). Therefore, the low correlation between ~~the~~ Fe_{sol}% and [nss-SO_4^{2-}]/[total Fe] of fine aerosol particles implied that ~~the~~ acidification of mineral dust was not the sole factor controlling Fe_{sol}%.

4. ~~The~~Establishment of source estimation method for d-Fe using the [d-Fe]/[d-Al] ratio

~~3.5.~~4.1. [d-Fe]/[d-Al] ratio in coarse aerosol particles and mineral dust

~~Thus,~~Correlation analysis between non-crustal Fe and d-Fe concentrations revealed that non-crustal Fe contributed to the source of d-Fe in fine aerosol particles but not in coarse aerosol particles. Correlation analysis is a simple method used to evaluate emission sources of d-Fe in aerosol particles~~, but~~. However, quantitative ~~estimation~~ estimations of the fraction of non-crustal Fe to d-Fe in aerosol particles present a challenge. Therefore, a quantitative indicator is preferable for the assessment of the relative abundance of non-crustal Fe to d-Fe ~~in aerosol particles is difficult. Therefore, it is preferable to have a quantitative indicator to assess the relative abundance of non-crustal Fe to d-Fe.~~. This study ~~challenged~~investigated the

evaluation of the ~~relative abundance~~fraction of non-crustal Fe to d-Fe using the [d-Fe]/[d-Al] ratio. One of the reasons is that ~~that~~ the [d-Fe]/[d-Al] ratio in mineral dust differs from that in non-crustal sources, as will be discussed below (Fig. ~~9a). In fact, the [d-Fe]/[d-Al] ratio in fine aerosol particles (average: 1.15 ± 0.803) was different from that in coarse aerosol particles (Fig. 9b, average: 0.408 ± 0.168).~~

~~Evaluating the relative abundance of non-crustal Fe to d-Fe in aerosol particles, it is necessary to generalize the [d-Fe]/[d-Al] ratios of crustal and non-crustal Fe. Therefore, we performed data compiles of the [d-Fe]/[d-Al] ratio in mineral dust and non-crustal Fe sources.~~6a). In addition, the [d-Fe]/[d-Al] ratio may vary depending on the extraction method ~~as well as the chemical weathering~~and aging process ~~in the atmosphere (Sholkovitz et al., 2012; Clough et al., 2019). Therefore, the data~~ of ~~[d-Fe]/[d-Al] were compiled considering not only the differences in the emission sources of Fe in aerosols but also the differences in the dissolution processes (i.e~~aerosol particles (Fig. 6a, e.g., proton-promoted ~~vs.~~versus ligand-promoted dissolutions). The ~~results are summarized in Fig. 9a.~~[d-Fe]/[d-Al] ratio in fine aerosol particles (ave.±1σ: 1.15 ± 0.80) differed from that in coarse aerosol particles (Fig. 6b, ave.±1σ: 0.408 ± 0.168). With the evaluation of the fraction of non-crustal Fe to d-Fe in aerosol particles, the [d-Fe]/[d-Al] ratios of crustal and non-crustal Fe can be generalized.

~~In the present study, we focused on biotite~~Biotite, illite, and Fe-rich chlorite ~~as the~~are considered representative mineral species of aluminosilicates in aerosol particles because ~~these aluminosilicates were~~they are detected in aerosol particles collected in East Asia (Takahashi et al., 2011; Kurisu et al., 2016a; Sakata et al., 2022). When Fe and Al in these aluminosilicates were ~~leached~~dissolved by proton-promoted dissolution (pH 1.0–7.0) under oxic conditions, the [d-Fe]/[d-Al] ratios of biotite, illite, and Fe-rich chlorite ~~was~~were within 0.427–0.930 (~~average:~~ave.±1σ: 0.776 ± 0.152), 0.156–0.689 (~~average:~~ave.±1σ: 0.404 ± 0.189), and 0.142–1.03 (~~average:~~ave.±1σ: 0.699 ± 0.303), respectively (Fig. ~~9a~~6a; Kodama and Schnitzer, 1973; Lowson et al., 2005; Bibi et al., 2015; Bray et al., 2015). In addition, the average [d-Fe]/[d-Al] ratios of Asian dust, Saharan dust, and Arizona test dusts obtained by proton-promoted dissolution were 0.238 ± 0.201, 0.163 ± 0.157, and 0.230 ± 0.009, respectively (Fig. 6a, Desboeufs et al., 2001; Duvall et al., 2008; Shi et al., 2011). The [d-Fe]/[d-Al] ratio ~~tended to decrease~~decreased with the increase in pH due to either or both the preferential retention of Fe in the mineral phase and precipitation of secondary ferrihydrite under near-neutral conditions (Fig. ~~S6~~S8, Kodama and Schnitzer, 1973; Desboeufs et al., 2001; Lowson et al., 2005; Bray et al., 2015). ~~In addition, the average [d-Fe]/[d-Al] ratios of Asian dust, Saharan dust, and Arizona test dust obtained by proton promoted dissolution were 0.238 ± 0.201, 0.163 ± 0.157, and 0.230 ± 0.00926, respectively (Fig. 8a, Desboeufs et al., 2001; Duvall et al., 2008; Shi et al., 2011). The [d-Fe]/[d-Al] ratio is also decreased with increasing pH (Fig. S6, Desboeufs, et al., 2001).~~ Thus, the [d-Fe]/[d-Al] ratio obtained from the proton-promoted dissolution of the mineral dust was between 0.~~1~~100 and 1.~~0~~00.

Organic ligands promote the dissolution of Fe from the mineral phase through the direct complexation of organic ligands with Fe at the mineral surface and ~~the~~ reduction ~~in~~of the saturation index of inorganic Fe in aqueous phase due to the formation of organic complexes of Fe ~~in solution~~ (Chen and Grassian, 2013; Paris and Desboefus, 2013; Wang et al., 2017). The [d-Fe]/[d-Al] ratios of biotite and Fe-rich chlorite associated with ligand-promoted dissolution were 0.795–3.83

(~~average:~~ave.±1σ: 1.20 ± 0.~~660~~66) and 1.19–1.37 (~~average:~~ave.±1σ: 1.31 ± 0.~~0629~~06), respectively (Kodama and Schnitzer, 1973; Bray et al., 2015). A previous study ~~found~~showed that the [d-Fe]/[d-Al] ratios of coarse aerosol particles extracted by 20 mmol~~/~~ L ~~of~~$^{-1}$ oxalate at pH 4.7 (1.31 ± 0.~~4184~~42) were higher than that of ~~MQ~~ultrapure water extraction (0.354 ± 0.714) (*Coarse aerosol (Proton) and Coarse aerosol (*~~Lignad~~*Ligand)* in Fig. ~~9a~~6a, Kurisu et al., 2019). Thus, the [d-Fe]/[d-Al] ratio associated with ligand-promoted dissolution was higher than that associated with proton-promoted dissolution (Fig. ~~8a~~6a). The higher stability constant (log *K*) of Fe^{3+} than that of Al^{3+} with organic ligands (e.g., log *K* of $AlC_2O_4^+$: 7.73, log *K* of $FeC_2O_4^+$: 9.15) ~~is a reason for~~caused the preferential dissolution of Fe over Al ~~by organic ligands, increasing~~from mineral dust, which increased the [d-Fe]/[d-Al] ratio.

The [d-Fe]/[d-Al] ratio of coarse aerosol particles ~~(~~collected by this study (n = 60, average: 0.121–0.927) was within ~~a~~the range of ~~the~~ [d-Fe]/[d-Al] ratios of mineral dust that underwent proton-promoted dissolutions ~~(Fig. 9b). In addition, the [d-Fe]/[d-Al] ratio of coarse aerosol particles~~, and it increased with the increase in Fe_{sol}% (Fig. ~~9b~~6b, r: 0.552). ~~Coarse aerosol particles with high~~ As previously mentioned, [d-Fe]/[d-Al] and Fe_{sol}% ~~yielded high nss-SO_4^{2-}/total Fe (Fig. 7a), indicating that coarse aerosol particles with high Fe_{sol}% underwent acidic conditions. This result~~obtained by proton-promoted dissolution of mineral dust increased with the decrease in pH, which is consistent with ~~a relationship of~~ the ~~[d-Fe]/[d-Al] ratio with dissolution pH.~~correlation between Fe_{sol}% and [nss-SO_4^{2-}]/[total Fe] in coarse aerosol particles (Fig. 4a). Therefore, the proton-promoted dissolution of mineral dust is the dominant source of d-Fe in coarse aerosol particles. ~~On the other hand~~By contrast, no coarse aerosol particles had [d-Fe]/[d-Al] ratios higher than 1.0 (Fig. ~~9b). Therefore,~~6b), which indicates that the effect of organic ligands on the solubilization of Fe and Al in coarse aerosol particles was ~~not significant.~~insignificant. In addition, the non-crustal Fe derived from road dust was not ~~factors~~a factor controlling the [d-Fe]/[d-Al] ratio in coarse aerosol particles due to ~~no~~the lack of correlation between the [d-Fe]/[d-Al] ratio and EF of Fe. This result is reasonable because the Fe_{sol}% of brake pads and tire wear debris ~~are~~was less than 0.01 % (Shupert et al., 2013; Halle et al., 2021).

~~3.6.~~4.2. ~~The~~ [d-Fe]/[d-Al] ratio in fine aerosol particles and their emissions

The average [d-Fe]/[d-Al] ratio of fine aerosol particles (n = 45, ~~average:~~ave.±1σ: 1.15 ± 0.~~803~~80, range: 0.386–4.67) was higher than ~~that~~those of coarse aerosol particles and mineral dust (Figs. ~~9a~~6a and ~~9b). In particular, the~~6b). The [d-Fe]/[d-Al] ratios of several fine aerosol particles exceeded 1.5, which was beyond the range of the ratio of mineral dust that underwent ligand-promoted dissolutions (Fig. ~~9a~~6a and ~~9b). Considering a~~6b). Given the good correlation between the [d-Fe]/[d-Al] ratio and EF of Fe (r: 0.505), the [d-Fe]/[d-Al] ratio higher than 1.5 was attributed to non-crustal Fe (Fig. ~~9c). Non~~6c). The non-crustal Fe in fine aerosol particles was derived from fly ash ~~of~~produced by high-temperature combustions, including steel/iron industrial processes, MSWI, and coal and fuel oil combustion. Fly ash contains two types of particles, namely, magnetic and non-magnetic particles (Kukier et al., 2003; Fomenko et al., 2021). ~~Since Fe and coexisted~~ Given the different elemental ~~concentrations~~compositions and Fe species ~~are different~~ of between magnetic and non-magnetic particles, the ~~impact~~influences of these particles on the [d-Fe]/[d-Al] ratio and Fe_{sol}% in fine aerosol particles were evaluated separately~~.~~

~~3.6.1.~~4.2.1. [d-Fe]/[d-Al] ratio of non-crustal Fe: magnetic particles

~~Mass~~The mass fraction of magnetic particles ~~was only~~accounts for a ~~few percent to~~small percentage of the total fly ash mass (Hansen et al., 1981), but up to 90 % ~~of~~Fe in fly ash ~~is~~was present as magnetic particles (Kukier et al., 2003). Iron species of magnetic particles in fly ash are mainly composed of ~~iron oxide~~Fe oxides, including hematite and magnetite. ~~Iron~~The iron concentration in magnetic particles ~~was~~reaches up to 60~~–~~ %~~–~~70 %, whereas that of Al ~~concentration in magnetic particles is~~ typically amounts to up to 10 % (Kukier et al., 2003; Fomenko et al., 2021). This result indicated that Fe in magnetic particles in fly ash can ~~be increased~~increase the EF of fine aerosol particles.

Previous studies have reported that d-Fe in fine aerosol particles yielded negative ~~Fe isotope ratio (~~δ^{56}Fe ~~< 0 ‰, (~~Kurisu et al., 2016a, 2019~~)~~), and ~~a~~ recent ~~study show~~research showed negative δ^{56}Fe in magnetic particles in $PM_{2.5}$ (Zuo et al., 2021). The magnetic particles in fine fractions (<1.0 μm) are considered ~~to be~~ formed by either or both the fragmentation of large particles and condensation of vaporized Fe. ~~In particular,~~The Fe-oxides ~~particles~~ formed by condensation of vaporized Fe (hereafter high-temp-FeOx) is ~~recognized as~~ one of the important sources of d-Fe in fine aerosol particles because the high-temp-FeOx yield negative ~~Fe isotope ratio caused~~δ^{56}Fe, which is formed by kinetic Fe isotope fractionation during vaporization ~~process~~ (Kurisu et al., ~~2016~~2016a, 2019). ~~In addition,~~The high-temp-FeOx can increase the [d-Fe]/[d-Al] ratio ~~in~~of fine aerosol particles because the [d-Fe]/[d-Al] ratio of fine aerosol particles with low δ^{56}Fe ~~(<~~ (<~1.0-‰) collected near a steel plant was higher than 1.5 when extracted with proton-~~promoted (MQ~~ (ultrapure water) and ligand-promoted (20 mmol/L oxalic acid at pH 4.7) dissolutions (*Anthropogenic Fe in fine aerosols (Proton) and Anthropogenic Fe in fine aerosols (Ligand)* in Fig. 6a; Kurisu et al., 2019). ~~Thus, high-temp-FeOx can increase the [d-Fe]/[d-Al] ratio of fine aerosol particles.~~ However, ~~Fe_{sol}% of~~ the Fe_{sol}% in magnetic particles in coal fly ash was less than 0.~~1~~100 % in weakly acidic solutions (Kukier et al., 2003), which was ~~much~~considerably lower than the Fe_{sol}% in fine aerosol particles (11.4 ± ~~6.97~~7.0 %). As previously mentioned, the Fe_{sol}% ~~of~~in fine aerosol particles ~~in fine aerosol particles~~ increased with the increase ~~with the increasing~~ in [nss-SO_4^{2-}~~/~~]/[total Fe] and with the decrease in aerosol pH (~~Fig. 7e~~Figs. 4c and ~~7e~~4e, respectively). In addition, ~~aerosol pH with~~at a high Fe_{sol}% (>10 ~~%)~~ %), the aerosol pH was ~~basically~~ lower than ~~10~~3.0, which was consistent with previous observations (Tao and Murphy, 2019b). Therefore, aerosol acidification is also ~~the~~a dominant factor ~~controlling~~that controls Fe_{sol}% in fine aerosol particles.

~~Ligand-promoted process may have partly enhanced Fe dissolution in mineral dust in~~As for fine aerosol particles with [d-Fe]/[d-Al] ~~ratios~~between 1.00 and 1.50, the effect of ~~1.0 to 1.5~~ligand-promoted dissolution of mineral particles should be considered (Fig. ~~9b~~6b). If ligand-promoted dissolution of mineral dust ~~in fine aerosol particles~~ is the dominant source of d-Fe in fine aerosol particles, ~~a good~~the correlation between ~~[~~the [d-Fe]/[d-Al] ratio and EF of Fe should not be observed because the EF of mineral dust ~~is~~should be about 1.~~0~~00. Therefore, ~~we conclude~~ the high [d-Fe]/[d-Al] ratio in fine aerosol particles was attributed to the presence of high-temp-FeOx rather than ligand-promoted dissolution of mineral dust.

~~3.6.2.~~4.2.2. ~~The~~ [d-Fe]/[d-Al] ratio of non-crustal Fe: non-magnetic fraction of fly ash

Non-magnetic particles are mainly composed of amorphous aluminosilicate glasses. The amorphous aluminosilicates, which are considered to be formed by the melting of crystalline aluminosilicate or chemical reactions of melted Al_2O_3 and SiO_2 (Zhang et al., 2007). TheAlthough previous studies did not perform the separation of magnetic and non-magnetic particles, the average [d-Fe]/[d-Al] ratio of coal and MSWI fly ash under acidic and circumneutral conditions was 0.104 ± 0.0751075 (Fig. 9a6a, Seidel and Zimmels, 1998; Praharaj et al., 2002; Kim et al., 2003; Huang et al., 2007; Chang et al., 2009; Gitari et al., 2009; Komonweeraket et al., 2015). These studies determined d-Fe and d-Al concentrations in fly ash without a separation between magnetic and non-magnetic particles. ConsideringGiven the high [d-Fe]/[d-Al] ratio in the magnetic particles, it is expected that mentioned above, the [d-Fe]/[d-Al] ratio of non-magnetic particles isshould be less than 0.1. However, no (Fig. 6a). Such a low [d-Fe]/[d-Al] ratio has not been detected in fine aerosol particles had, which indicates that non-magnetic aluminosilicate glass in fly ash is not a [dominant source of d-Fe]/[d-Al] ratio less than 0.1 (Fig. 9b). In addition, non-magnetic aluminosilicates of coal combustions and MSWI could not increase the EF of Fe in fine aerosol particles because (Fig. 6b). Furthermore, the EF of Fe in non-magnetic aluminosilicate glass emitted from MSWI and coal fly ash is almost 1, which cannot explain the correlation between EF and Fe_{sol}% for these ashes was almost 1 particles (Sakata et al., 2022; Li et al., 2022). Therefore, the non-magnetic aluminosilicatesaluminosilicate glass derived from coal combustion and MSWI were unlikely theis possibly not a dominant source of aerosol particles with high Fe_{sol}% and [d-Fe]/[d-Al] ratiosratio in fine aerosol particles.

In the case of heavy-oil combustion, Fe_{sol}% in oil fly ash can reach 80 % under circumneutral pH conditions because ofdue to the presence of water-soluble Fe(III)-sulfate (Schroth et al., 2009; Oakes et al., 2012). DespiteIn addition, the fly ash emitted from heavy-oil combustions may be a source of d-Fe in fine aerosol particles collected in summer. Despite the limited data, the [d-Fe]/[d-Al] ratios of oil fly ash werereached 0.403, 1.07, and 7.00 at pH 5.7, 4.7, and −0.3, respectively (Akita et al., 1995; Desboeufs et al., 2001). Assuming With the assumption of a linear relationship between the dissolution pH of heavy oil fly ash and the [d-Fe]/[d-Al] ratio of heavy-oil fly ash, the expected [d-Fe]/[d-Al] ratio of heavy-oil ash was approximately 4.0 at the average aerosol pH in fine aerosol particles collected in summer (average: 2.11 ± 0.4522345). However, it is difficult to explainheavy oil fly ash was not the reason for the correlation between the [d-Fe]/[d-Al] ratio and EF of Fe in source of fine aerosol particles with high EF of Fe and [d-Fe]/[d-Al] ratio because the EF of Fe in heavy-oil fly ash was almost 1.0 as well as non-magnetic aluminosilicates of coal and MSWI (Sakata et al., 2017). Therefore, it is considered that the contribution of fly ash emitted from heavy oil combustion is not large.

3.7.4.3. Fractions of crustal Fe and high-temp-FeOx in d-Fe and their Fe_{sol}%

3.7.1.4.3.1. Estimation method for the fractions of crustal and high-temp-FeOx and their Fe_{sol}%

The fractions of mineral dust and non d-Fe derived from crustal Fe and high-temp-FeOx in d-Fe in fine aerosol particles were estimated based on the [d-Fe]/[d-Al] ratio of fine aerosol particles. The [d-Fe]/[d-Al] ratios of crustal Fe and non-crustal Fe were set to values generalized from the results obtained in this study. The average [d-Fe]/[d-Al] ratio of coarse aerosol particles was 0.408, which was within the range of the ratios of aluminosilicates and loess samples in the references (Fig. 9a

and 9b). In the case of non-crustal Fe, we only focused on high-temp-FeOx because the fine aerosol particles did not exhibit the low [d-Fe]/[d-Al] ratio attributed to non-magnetic aluminosilicates of coal combustions and MSWI ([d-Fe]/[d-Al] < 0.1, Fig. 9a). However, the [d-Fe]/[d-Al] ratio of high-temp-FeOx has not been reported. Therefore, two [d-Fe]/[d-Al] ratios of pyrogenic FeOx were used in the calculation: the non-crustal [d-Fe]/[d-Al] ratio of 4.67, which was the highest [d-Fe]/[d-Al] ratio of fine aerosol particles. Another is the average [d-Fe]/[d-Al] ratio of 2.08 of fine aerosol particles with [d-Fe]/[d-Al] ratios higher than 1.5.

In consideration of the binary mixing of d-Fe in crustal d-Fe and high-temp-FeOx (crustal-dFe and high-temp-FeOx-dFe), the fraction of high-temp-FeOx-dFe in d-Fe were estimated by using the following equations:

$$f_{\text{crustal-dFe}} + f_{\text{high-temp-FeOx-dFe}} = 1, \text{ (Eq. 7)}$$

$$[\text{d-Fe}]/[\text{d-Al}]_{\text{aerosol}} = ([\text{d-Fe}]/[\text{d-Al}])_{\text{crust}} \times f_{\text{crustal-dFe}} + ([\text{d-Fe}]/[\text{d-Al}])_{\text{non-crust}} \times f_{\text{high-temp-FeOx-dFe}}, \text{ (Eq. 8)}$$

where $f_{\text{crustal-Fe}}$ and $f_{\text{high-temp-FeOx-dFe}}$ are. Hereafter, the fractions of d-Fe derived from crustal Fe and high-temp-FeOx are denoted as F_{crust} and F_{anthro}, respectively. $([\text{d-Fe}]/[\text{d-Al}])_{\text{aerosol}}$, $([\text{d-Fe}]/[\text{d-Al}])_{\text{crustal-Fe}}$, and $([\text{d-Fe}]/[\text{d-Al}])_{\text{high-temp-FeOx-dFe}}$ are the molar [d-Fe]/[d-Al] ratios of aerosol particles, crustal Fe, and high-temp-FeOx, respectively. In addition, the $f_{\text{high-temp-FeOx-dFe}}$ of TSP (= coarse + fine aerosol particles) was estimated by using the [d-Fe]/[d-Al] ratio of TSP. For the comparison of the $f_{\text{high-temp-FeOx-dFe}}$ of TSP, the relative abundance of non-crustal d-Fe in fine aerosol particles to that of d-Fe in TSP samples ($f_{\text{high-temp-FeOx-dFe-fine/TSP}}$) was calculated by using the following equationIn consideration of the binary mixing of d-Fe derived from mineral dust and high-temp-FeOx, the F_{anthro} in fine aerosol particles and F_{anthro} in TSP ($F_{anthro\text{-}TSP}$) were estimated with the following equations:

$$(f_{\text{high-temp-FeOx-dFe/TSP}}) = \Sigma(f_{\text{high-temp-FeOx-dFe}} \times [\text{d-Fe}])_{\text{fine}} / [\text{d-Fe}]_{\text{TSP}}, \text{ (Eq. 9)}$$

where $\Sigma(f_{\text{high-temp-FeOx-dFe}} \times [\text{d-Fe}])_{\text{fine}}$ is the summation of non-crustal d-Fe concentration in fine aerosol particles (<1.3 μm). The $f_{\text{high-temp-FeOx-dFe/TSP}}$ calculated by using Equation 9 was almost identical to the $f_{\text{non-crustal-Fe}}$ of TSP calculated by using Equations 7 and 8 (Fig. S7). This result provided evidence that the coarse aerosol particles contained low amounts of non-crustal d-Fe that increased the [d-Fe]/[d-Al] ratio of TSP.

3.7.2. The fraction of high-temp-FeOx to d-Fe

The calculation showed that the $F_{crust} + F_{anthro} = 1$, (Eq. 7)

$$[\text{d-Fe}]/[\text{d-Al}]_{\text{aerosol}} = ([\text{d-Fe}]/[\text{d-Al}])_{\text{crust}} \times F_{crust} + ([\text{d-Fe}]/[\text{d-Al}])_{\text{anthro}} \times F_{anthro}, \text{ (Eq. 8)}$$

where $([\text{d-Fe}]/[\text{d-Al}])_{\text{aerosol}}$ is the [d-Fe]/[d-Al] ratio in aerosol particles. The $([\text{d-Fe}]/[\text{d-Al}])_{\text{crust}}$ and $([\text{d-Fe}]/[\text{d-Al}])_{\text{anthro}}$ are the representative values of [d-Fe]/[d-Al] ratios of mineral dust and anthropogenic Fe, respectively. Here, the $([\text{d-Fe}]/[\text{d-Al}])_{\text{crust}}$ and $([\text{d-Fe}]/[\text{d-Al}])_{\text{anthro}}$ were defined based on our observational results. The average [d-Fe]/[d-Al] ratio in coarse aerosol particles (0.408) was used as a representative $([\text{d-Fe}]/[\text{d-Al}])_{\text{crust}}$, and its value was within the range of proton-promoted dissolution of mineral dust (Figs. 6a and 6b). Given that the $([\text{d-Fe}]/[\text{d-Al}])_{\text{anthro}}$ has not been reported by previous studies, its two types were used in the calculation. The $([\text{d-Fe}]/[\text{d-Al}])_{\text{anthro}}$ was 4.67, which was the highest value observed in fine aerosol particles. Another $([\text{d-Fe}]/[\text{d-Al}])_{\text{anthro}}$ was the average [d-Fe]/[d-Al] ratio of fine aerosol particles with [d-Fe]/[d-Al] ratios

higher than 1.5. At this time, the $([d\text{-}Fe]/[d\text{-}Al])_{anthro}$ was 2.08. When the average [d-Fe]/[d-Al] was used for the calculation, the F_{anthro} was higher than the value calculated by the highest$([d\text{-}Fe]/[d\text{-}Al]_{anthro}$ (Figs. S9a and S9b). F_{anthro} was calculated using the average $([d\text{-}Fe]/[d\text{-}Al])_{anthro}$ to avoid underestimation.

Finally, the Fe_{sol}% of crustal and high-temp-FeOx (crustal-Fe_{sol}% and anthro-Fe_{sol}%) in fine aerosol particles were estimated through the following equations:

$$\text{Crustal-}Fe_{sol}\% = [(\text{d-Fe} \times F_{crustal})/\text{crustal Fe}] \times 100, \text{ (Eq. 9)}$$

$$\text{Anthro-}Fe_{sol}\% = [(\text{d-Fe} \times F_{anthro})/\text{non-crustal Fe}] \times 100. \text{ (Eq. 10)}$$

Crustal and non-crustal Fe concentrations were calculated using Eqs. 3 and 4, respectively.

4.3.2. Size dependence and seasonal variation of F_{anthro}

The annual average ~~of the fractions of non-crustal Fe in d-Fe in~~ $F_{anthro\text{-}TSP}$ was 19.9 ± 19.2 % (Fig. ~~10a~~7a, range: 1.48–80.7 %). ~~The fraction of non-crustal Fe calculated with the [d-Fe]/[d-Al] ratio of 4.67 was lower than that calculated~~ The $F_{anthro\text{-}TSP}$ was higher in summer–fall with the ~~[d-Fe]/[d-Al] ratio of 2.08 (Figs. S8a and S8b). High non-crustal Fe fractions were observed in summer and fall~~ influence of Japanese air mass (average: 29.4 ± 25.8 %, range: 9.41–80.7 %) ~~when the air mass originated from the domestic region (Fig. S1). By contrast, non-crustal Fe (~~than in winter–spring with the influence of Asian outflow (Fig. 7a, average: 13.5 ± 10.6 %, range: 1.48–34.4 ~~%) in winter and spring, when air masses originated from East Asia, was lower than that~~%). The high $F_{anthro\text{-}TSP}$ in summer ~~and~~ was attributed to the high EF of Fe and [d-Fe]/[d-Al] ratio in the season. From the viewpoint of size dependence of F_{anthro}, the largest F_{anthro} in summer–fall~~. A satellite-based observation reported that~~ and winter–spring was found in the finest and 0.39–0.69 μm fractions, respectively (Fig. 7b). These results are consistent with the source apportionment of Fe using $\delta^{56}Fe$ at the same sampling site because (i) the contribution of anthropogenic Fe to d-Fe in fine aerosol particles was more significant in summer than in spring due to the low $\delta^{56}Fe$, and (ii) the lowest $\delta^{56}Fe$ was found in the finest and 0.39–0.69 μm fractions in summer and spring, respectively. Thus, the source estimation of Fe using [d-Fe]/[d-Al] is consistent with that which uses $\delta^{56}Fe$.

Given the Fe supply to the Pacific Ocean, spring is the most important season throughout the year because approximately half of aerosol transport events from East Asia to the Pacific Ocean occurred in spring between 2007 and 2016 ~~occurred in spring~~, and ~~that dust~~ they were mainly associated with mineral dust events ~~mainly occurred in spring~~ (Zhu, Q., 2020). In addition, atmospheric Fe is supplied to the surface ocean by an episodic dust event that accounts for approximately 30~~–~~ %~~–~~ 90 % of annual Fe depositions within 5 % of the days ~~of~~in a year (Mahowald et al., 2009). In consideration of these ~~phenomena~~facts with the estimation results of $F_{anthro\text{-}TSP}$ and $F_{crust\text{-}TSP}$, mineral dust was the dominant source of d-Fe in aerosol particles deposited in the North Pacific Ocean~~.~~ (Fig. 7a). Nevertheless, the contribution of high-temp-FeOx, as a source of d-Fe in surface seawater during dust events, cannot be ~~negligible~~disregarded because the average fraction of non-crustal Fe during spring and dust events was 10.2 ± 7.~~58~~6 %.

~~On the basis of the fractions of crustal and non-crustal Fe, the Fe_{sol}% of crustal and non-crustal Fe in fine aerosol particles were estimated by using following equations:~~

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4.3.3. Crustal-Fe_{sol}% ~~= [(d-Fe × $f_{crustal\text{-}dFe}$)/crustal Fe] × 100, (Eq. 10)~~**and anthro-Fe_{sol}%**

~~High-temp-FeOx-Fe_{sol}% = [(d-Fe × $f_{high\text{-}temp\text{-}FeOx\text{-}dFe}$)/non-crustal Fe] × 100. (Eq. 11)~~

~~Crustal and non-crustal Fe concentrations were calculated by using Equations 3 and 4, respectively.~~ The annual average crustal-Fe_{sol}% ~~and non-crustal-Fe_{sol}% of fine aerosol particles were~~(ave.±1σ: 14.1 ~~% (0–43.7 %) and 9.35 % (0.501–46.2 %),~~
650 ~~respectively (Figs. 8c and 8d). The average crustal-Fe_{sol}% of TSP was 6.52 ± 3.05 % ([d-Fe]/[d-Al]: 2.08) because insoluble Fe in mineral dust was mainly distributed in coarse aerosol particles. When the [d-Fe]/[d-Al] ratio was set to 4.67, the crustal-Fe_{sol}% and non-crustal-Fe_{sol}% of fine aerosol particles were 20.2 % (0.0285–65.1 %) and 4.62 % (0.209–35.9 %), respectively (Figs. S8c and S8d). The~~ ± 9.3 %) was higher ~~value of crustal~~than the anthro-Fe_{sol}% (ave.±1σ: 9.35 ± 10.29 %) when the ~~[d-Fe]/[d-Al] ratio was set to 4.67 than that when the [d-Fe]/[d-Al] ratio was set to 2.08 was due to the large contribution of~~
655 ~~crustal Fe to d-Fe. Thus, when focusing~~ focus was on fine aerosol particles (Figs. 7c and 7d). ~~, mineral dust showed higher Fe_{sol}% than high-temp FeOx. One reason is that high-temp FeOx was derived from local~~ This result is inconsistent with the finding of previous studies where the Fe_{sol}% of anthropogenic ~~emissions and may not have undergone considerable chemical aging. Another possible reason~~Fe derived from high-temperature combustion was higher than that of mineral dust (Sedwick et al., 2007; Sholkovitz et al., 2009). One of the reasons is that the Fe oxide nanoparticles were poorly solubilized at the aerosol
660 pH of the samples obtained in this study. Marcotte et al. ~~1.7 and 4.3,~~ (2020) showed that the Fe_{sol}% of submicron Fe–oxides (<1.5 %) was lower than ~~that~~those of submicron illite and kaolinite (about ~~Marcotte et al. 2020). As previously mentioned, fine aerosol particles with high Fe_{sol}% (>~~10 %) ~~experienced highly acidic conditions (pH < 3.0). Therefore,~~ %). Similar results have been obtained from the ~~high-Fe_{sol}% shown by mineral dust in non-crustal Fe in fine aerosol particles is consistent with the results of laboratory~~ experiments ~~(Marcotte et al. 2020). The Fe_{sol}% of fine aerosol particles~~ on Fe dissolution from
665 aluminosilicates and Fe-oxides at pH 2.0 (particle diameter < 100 μm, Journet et al., 2008). According to the results of this study, the aerosol pH of fine aerosol particles with high Fe_{sol}% (>10 %) was lower than 3.0, but almost no fine aerosol samples whose aerosol pH was lower than 1.7 was observed (Fig. 4e). Therefore, even if the Fe-oxides were derived from high-temperature combustion, the significant increase in their anthro-$Fe_{sol\%}$ was unlikely without sufficient acidification. Another reason is that mineral dust with a low Fe_{sol}% was mainly present in coarse aerosol particles. The annual average of crustal-
670 Fe_{sol}% in TSP was 6.52 ± 3.05 %, which was lower than that of anthro-Fe_{sol}%.

The crustal-Fe_{sol}% of fine aerosol particles in the 0.39–0.69 and 0.69–1.3 μm fractions were higher than that in the finest fraction throughout the year (Fig. ~~6e), indicating~~7c), which indicates that mineral dust in the 0.39–0.69 and 0.69–1.3 μm fractions was more aged than that in the finest fraction. ~~Single-particle analyses of aerosol particles in East Asia showed that the abundance of the~~ This result is reasonable because internally mixed particles of Fe and sulfate were found in the fine
675 aerosol particles, whose number fraction relative to the total number of Fe-bearing particles ~~with sulfate was~~became the

~~highest~~largest at ~~approximately 0.7 μm of aerosol diameter~~around 700 nm rather than finer than 400 nm (Sullivan et al., ~~2007a~~2007; Li et al., 2017; Zhu, Y. et al., 2020, 2022). ~~In addition, Fe_{sol}%~~The uptake of Fe-bearing particles into cloud water promotes internal mixing with sulfate (Li et al., 2017; Liu et al., 2018; Lin et al., 2019). However, the sufficient dissolution of Fe in fine aerosol particles at the pH condition of ~~mineral dust~~cloud water is unlikely (global average pH: 5.2, Shah et al., 2020), as observed in the ~~0.39–0.69 and 0.69–1.3 μm fractions collected in the Pacific Ocean were higher than that in coarse~~relationship between aerosol ~~particles due to chemical aging via condensation–evaporation~~pH and Fe_{sol}% (Fig. 4e). The aerosol pH decreased rapidly with the phase transition from cloud water to the aerosol concentration of protons in a tiny amount of aerosol liquid water content. Furthermore, the uptake coefficient of SO_2 by aluminosilicates increases as they experience cloud processes, which is expected to further promotion of aerosol acidifications (Wang et al., 2019). Considering these facts, crustal-Fe_{sol}% in fine aerosol particles was enhanced by the aerosol–cloud water cycle during transport ~~(Sakata et al., 2022). Therefore, the chemical aging of mineral dust in fine aerosol particles plays an important role in the supply of Fe to the ocean surface.~~.

~~4.~~5. Implication for marine aerosol particles

The availability of the [d-Fe]/[d-Al] ratio for ~~evaluating~~ the ~~emission sources~~evaluation of ~~d-Fe~~F_{crust} and F_{anthro} in marine aerosol particles was investigated ~~by~~ using the observational results of previous studies (Buck et al., 2006, 2010b; Shelley et al., 2018; Baker et al., 2020; Sakata et al., 2022). In general, soluble metals in aerosol particles were extracted ~~by using MQ~~with ultrapure water through instantaneous or batch leaching, and only Baker et al. (2020) ~~employed~~used ammonium acetate solution with ~~a~~ pH ~~of~~ 4.7. The [d-Fe]/[d-Al] ratio of the marine aerosol samples collected in the Pacific and Atlantic Oceans were rarely higher than 1.0 (~~Fig. 11a~~Figs. 8a and ~~11b~~8b). The ~~fractions of non-crustal d-Fe in~~F_{anthro} of TSP collected from the Atlantic and Pacific Oceans were 9.58 % and 13.4 %, respectively (Fig. ~~11c~~8c). In the Pacific Ocean, ~~the contribution of non-crustal d-Fe tends to be~~F_{anthro} was higher in the region east of 170 °E because anthropogenic Fe in fine aerosol particles ~~is~~was transported farther than that in coarse mineral dust particles (Fig. ~~12a~~9a, Mahowald et al., 2018). By contrast, the large ~~fraction of anthropogenic Fe~~F_{anthro} in the Atlantic was ~~found~~detected around the coastal ~~area~~areas in North America and Europe (Fig. ~~12b~~9b). This result was consistent with the estimation of the ~~non-crustal Fe fraction~~F_{anthro} based on δ^{56}Fe, which indicated that more than half of the d-Fe in Fe around the coastal regions was derived from anthropogenic Fe with a negative δ^{56}Fe (Conway et al., 2019). However, the ~~fraction~~F_{anthro} of ~~non-crustal Fe in~~ TSP with negative δ^{56}Fe values, which were estimated on the basis of the [d-Fe]/[d-Al] ratio, was 12.4 ± 2.9 % (Fig. 8c). Thus, the F_{anthro} estimated by the [d-Fe]/[d-Al] ratio ~~was only 12.4 ± 2.92 % (Fig. 11c). Thus, a discrepancy existed between the results of d-Fe emission source estimates based on Fe isotopic ratios and those based on [d-Fe]/[d-Al].~~differed from that estimated by δ^{56}Fe. One of the reasons ~~is~~ for this discrepancy ~~is~~was the limited data ~~on~~of the [d-Fe]/[d-Al] and δ^{56}Fe ratios ~~of~~for emission source samples, ~~in particular~~specifically anthropogenic emissions. The [d-Fe]/[d-Al] ratio and δ^{56}Fe of high-temp-FeOx were estimated based on the ~~basis of the~~ measurement values of aerosol particles~~. The~~ due to the lack of reliable reference materials for high-temp-FeOx. By contrast, the [d-Fe]/[d-Al]

ratios of mineral dust and non-magnetic aluminosilicates of coal combustion and MSWI had a small effect on the uncertainty of F_{anthro} estimation due to the ~~non-crustal Fe fraction estimates because measured~~presence of reference values ~~were available~~. Therefore, further studies involving the accumulated data on the [d-Fe]/[d-Al] ratio and δ^{56}Fe of high-temp-FeOx collected from various industrial sites are required. Currently, the accurate δ^{56}Fe and [d-Fe]/[d-Al] ratio of high-temp-FeOx may be obtained through the separation of magnetic particles, as performed by Zuo et al. (2022). The accumulated data on the previously reported values of [d-Fe]/[d-Al] ratio can be used and are expected to provide ~~insight~~insights into the time-series variation in the contribution of anthropogenic Fe to aerosols in marine aerosols.

Figure ~~11b~~8b shows a scatter plot of the [d-Fe]/[d-Al] ratios and Fe_{sol}% of size-fractionated aerosol particles collected from the Atlantic and Pacific Oceans (Baker et al., 2020; Sakata et al., 2022). The average [d-Fe]/[d-Al] ratios of coarse and fine aerosol particles collected offshore of the Sahara Desert were 0.216 ± 0.163 and 0.155 ± 0.~~0549~~055, respectively. These values were similar to the [d-Fe]/[d-Al] ratio of Saharan dust (0.108 ± 0.~~0609), indicating~~061), which indicates that the d-Fe in these size-fractionated aerosol samples originated from Saharan dust. Iron in the size-fractionated aerosol particles collected in the western Pacific Ocean was also derived from mineral dust regardless of aerosol diameter because the EF of Fe in all size fractions was almost 1.00 (Sakata et al., 2022). The average [d-Fe]/[d-Al] ratio of coarse aerosol particles collected above the Pacific Ocean (0.378 ± 0.104) was slightly higher than the average [d-Fe]/[d-Al] ratio of Asian dust (0.238 ± 0.201) but was similar to ~~the ratio~~that of coarse aerosol particles collected in this study (0.408 ± 0.168). Therefore, the d-Fe in these samples was derived from the hydrolysis or proton-promoted dissolution of mineral dust. Although the Fe in coarse aerosol particles collected in the Atlantic and Pacific Oceans was derived from mineral dust, the [d-Fe]/[d-Al] ~~ratio~~ratios of the coarse and fine aerosol particles above the Atlantic Ocean ~~was~~were lower than that of coarse aerosol particles collected in the Pacific Ocean. The differences in ~~the~~ mineralogical compositions of mineral dust in the hinterlands account for ~~the~~ differences in the ratios of ~~the~~ aerosol particles collected in the Atlantic and Pacific Oceans. Therefore, ~~measuring~~measurement of the [d-Fe]/[d-Al] ratio of soil samples around the sampling site is important to determine the representative [d-Fe]/[d-Al] ratio of mineral particles in aerosol particles.

The high Fe_{sol}% (>10 %) of fine aerosol particles in the Pacific was attributed to ferric organic complexes of humic-like substances (Fe(III)-HULIS, Sakata et al. 2022). The [d-Fe]/[d-Al] ratio of fine aerosol particles containing Fe(III)-HULIS ~~is~~was expected to be between 1.0 and 1.5 due to ligand-promoted dissolution. However, the obtained [d-Fe]/[d-Al] ratio ~~of fine aerosol~~for these particles ~~containing Fe(III) HULIS~~ was 0.440 ± 0.117 (range: 0.255–0.567), which was consistent with the ratio of Asian dust that underwent proton-promoted dissolution. A previous study reported that ~~the Fe_{sol}% of these samples was enhanced by the~~ aerosol acidification of aluminosilicates enhanced the Fe_{sol}% of samples; Fe(III)-HULIS then formed via complexation reactions in cloud water (Sakata et al., 2022). ~~Thus, the~~The [d-Fe]/[d-Al] ratio may not change even if the Fe species was altered by atmospheric processes after Fe solubilization. However, ~~this point needs~~ further investigation~~. The~~ of this point is required. Moreover, to evaluate source and dissolution processes using the [d-Fe]/[d-Al] ratio, we preferred the determination of the [d-Fe]/[d-Al] ratio via ~~MQ~~ultrapure water extraction without organic ligands (e.g., oxalate and acetate) ~~is preferred for investigating the contribution of ligand-promoted dissolution to Fe_{sol}% enhancement~~ because the ratio is altered

if the extracted solution contains organic ligands (e.g., coarse aerosol ~~[~~(P~~] vs.~~) versus coarse aerosol ~~[~~(L~~],~~), Fig. ~~9a). However,~~6a). The data on the [d-Fe]/[d-Al] ratio of size-fractionated marine aerosol particles under the effect of high-temp-FeOx up to this point have not ~~yet~~ been published ~~at this time.~~. Therefore, further studies on the [d-Fe]/[d-Al] ratio of marine aerosol particles influenced by high-temp-FeOx are required. If future studies detect high [d-Fe]/[d-Al] ratios in marine aerosol samples that are strongly affected by high-temp-FeOx, then the [d-Fe]/[d-Al] ratio will be a powerful tool for ~~estimating~~estimation of the fraction of crustal and non-crustal Fe in d-Fe in marine aerosol particles.

~~5.~~6. Conclusion

Annual observations ~~were conducted on~~of the total and ~~dissolved~~ d-Fe and Al concentrations in size-fractionated aerosol particles~~. Total~~ were conducted at the eastern end of East Asia. The total Fe and Al concentrations were mainly distributed in coarse aerosol particles, whereas d-Fe and d-Al concentrations dominated ~~in~~ fine aerosol particles. ~~Considering~~Given the higher d-Fe concentration and longer residence time of fine aerosol particles than ~~those of~~ coarse aerosol particles, the atmospheric deposition of fine aerosol particles was the dominant source of d-Fe in the surface ocean. ~~Since the~~The [d-Fe]/[d-Al] ratio of coarse aerosol particles (0.408 ± 0.168) was lower than that of fine aerosol particles (1.15 ± 0.~~803),~~80). Thus, the sources of d-Fe differed between coarse and fine aerosol particles. The [d-Fe]/[d-Al] ratio of coarse aerosol particles was similar to that observed ~~of~~for Fe dissolved via proton-promoted dissolution. ~~Indeed,~~The Fe_{sol}% increased as the surfaces of coarse particles became hygroscopic through the reaction with sulfuric acid. This effect intensified with the reduction in particle size. The fine aerosol particles presented a wide range of [d-Fe]/[d-Al] ratios (0.386–4.67). The correlation of the [d-Fe]/[d-Al] ratio of the fine aerosol particles with the EF of Fe indicated that the high [d-Fe]/[d-Al] ratios (>1.5) ~~could~~can be attributed to non-crustal Fe. High-temp FeOx in magnetic particles ~~was~~were likely the dominant species ~~in~~of non-crustal Fe with high [d-Fe]/[d-Al] ratios. The ~~fractions of mineral dust~~F_{crust} and ~~high-temp-FeOx~~F_{anthro} were evaluated ~~on the basis of~~using the [d-Fe]/[d-Al] ratios ~~and emission sources of~~ in aerosol particles~~.~~ and their emission source samples. Approximately 80 % of d-Fe in TSP collected in spring, when numerous ~~events of~~ aerosol transport events from East Asia to the North Pacific occurred, originated from mineral particles. The high ~~fraction of mineral dust~~F_{crust} was attributed to the higher crustal-Fe_{sol}% ~~of crustal Fe~~ than ~~that of high-temp-FeOx.~~anthro-Fe_{sol}%. The Fe_{sol}% of submicron mineral dust (e.g., illite) was ~~known to be~~ higher than ~~that~~those of hematite and magnetite of the same size ~~under acidic conditions.~~in solutions with pH higher than 1.7. Furthermore, the Fe_{sol}% of fine aerosol particles increased with the decrease in aerosol pH, ~~indicating~~which indicates that the acidification of mineral particles played an important role in the supply of d-Fe to surface seawater in the North Pacific via atmospheric deposition. Thus, the source estimation of d-Fe ~~by~~ using the [d-Fe]/[d-Al] ratio is a powerful tool for ~~estimating~~estimation not only of the source of d-Fe in marine aerosols but also the dissolution processes of Fe in aerosol particles. The source estimation of d-Fe ~~by~~ using the [d-Fe]/[d-Al] ratio also has the advantage of being performed through a simple analytical method, in which Fe and Al are extracted by ~~using MQ~~ultrapure water, and their concentrations are measured through ICP–MS. Therefore, this method can be easily conducted not only in future studies but also on aerosol samples

collected in previous ~~studies~~research. Currently, data on the [d-Fe]/[d-Al] ratios of aerosols ~~that~~, which are strongly affected by anthropogenic Fe and emission sources associated with high-temperature combustion processes, are limited. Therefore, ~~collecting~~collection of data on the [d-Fe]/[d-Al] ratios of these samples will enable us to identify the emission sources of d-Fe in marine aerosol particles with increased robustness.

Data Availability All quantitative data will be available at the ERAN database (https://www.ied.tsukuba.ac.jp/database/00156.html) with a doi: 10.34355/CRiED.U.Tsukuba.00156.

Supplement. The supplement related to this article is available online at XXXX.

Author contributions. The study was designed by K.S., A.S., and Y.T. Aerosol sampling was performed by K.S. and Y.Y. Major ion concentrations were determined by K.S., Y.Y., and C.M. Trace metal concentrations were measured by K.S., C.M., and M.K. The paper was written by K.S., and Y.T., and all authors were reviewed the manuscript before submission.

***Competing interests*.** The authors declare that they have no conflict of interest.

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Figure captions

Figure 1: Sites (Higashi-Hiroshima) of size-fractionated aerosol sampling. Maps were visualized by Ocean Data View (Schlitzer, 2021).

Figure 2: Monthly variations and size distributions of ~~(a) Na^+, (b) Ca^{2+}, (c) Mg^{2+}, (d) K^+, (e) NH_4^+, (f) Cl^-, (g) NO_3^-, (h) SO_4^{2-}, and (i) nss-SO_4^{2-}. The summation of all fractions corresponds to TSP concentration~~the (a) total Al and (b) total Fe concentrations. (c) Box plot of EF in each size fraction.

Figure 3: Monthly variation and size distributions of (a) d-Fe and (b) Fe_{sol}%. (c) Box plot of Fe_{sol}% in each size fraction. Monthly variation and size distributions of (d) d-Al and (e) Al_{sol}%. (f) Box plot of Al_{sol}% in each size fraction.

~~Figure 3: Monthly variations and size distributions of (a) total Al and (b) total Fe concentrations. (c) Box plot of Fe_{sol}% in each size fraction.~~

Figure 4: Scatter plots of ~~non-crustal Fe concentration with (a) Cu, (b) Zn, (c) Sb, and (d) Pb~~Fe_{sol}% and Al_{sol}% in coarse aerosol particles with (a) [nss-SO_4^{2-}]/[total Fe] and [nss-SO_4^{2-}]/[total Al] and (b) [NO_3^-]/[total Fe] and [NO_3^-]/[total Al]. Scatter plots of Fe_{sol}% and Al_{sol}% in fine aerosol particles with (c) [nss-SO_4^{2-}]/[total Fe] and [nss-SO_4^{2-}]/[total Al] , (d) [NO_3^-]/[total Fe] and [NO_3^-]/[total Al] and (e) aerosol pH.

Figure 5: Scatter plots of ~~non-crustal Fe concentration~~d-Fe with (a) ~~Zn~~non-crustal Fe, (b) ~~Sb~~total V, (c) ~~Pb, and (d) V~~total Cu, (d) total Sb, and (e) total Pb concentrations in fine aerosol particles.

Figure 6: (a) Box plot of [d-Fe]/[d-Al] in emission source samples (Proton) and (Ligand) indicating proton- and ligand-promoted dissolutions. Scatter plots of the [d-Fe]/[d-Al] ratio with (b) the Fe_{sol}% and (c) EF of Fe. Light blue circles and black squares in panels (b) and (c) represent the data on coarse and fine aerosol particles collected in Higashi-Hiroshima, respectively. Pink, yellow, light green, and gray regions show the typical ranges of the [d-Fe]/[d-Al] ratios of aluminosilicate glasses of coal combustion and MSWI, the proton- and ligand-promoted dissolution of mineral dust, and high-temp-FeOx, respectively. The regions were decided based on the box plots of panels (a).

Figure 7: Monthly variations of (a) non-crustal Fe fraction in TSP and (b) non-crustal Fe fraction in fine aerosol particles, (c) crustal-Fe_{sol}%, and (d) non-crustal Fe_{sol}% when the [d-Fe]/[d-Al] ratio of non-crustal Fe is 2.08. The yellow shaded region shows the period when the air mass was mainly derived from Japan.

Figure 8: Scatter plots of the [d-Fe]/[d-Al] ratio with Fe_{sol}% in (a) TSP samples and (b) size-fractionated aerosol particles collected in the marine atmosphere. (c) The fraction of non-crustal d-Fe in these samples was calculated using Equations 6 and 7. The [d-Fe]/[d-Al] ratios of mineral dust in the Pacific and Atlantic Oceans were the average ratios of Asian (0.238) and Saharan dusts (0.163), respectively. The [d-Fe]/[d-Al] ratio of non-crustal Fe was fixed at 2.08. The [d-Fe]/[d-Al] ratios of the TSP and size-fractionated aerosol samples were adapted from the works of Buck et al. (2006, 2010b), Shelley et al. (2018), Baker et al. (2020), and Sakata et al. (2022). The Fe isotopic ratio of TSP in the Atlantic Ocean was reported by Conway et al. (2019). Pink, yellow, light green, and gray regions in panels (a) and (b) show the typical [d-Fe]/[d-Al] ratios of coal/MSWI fly ash, proton- and ligand-promoted mineral dust dissolutions, and pyrogenic Fe oxides, respectively.

Figure 9: Non-crustal Fe fractions in the TSP samples collected from (a) the Pacific Ocean and (b) Atlantic Ocean. Non-crustal Fe fractions were calculated using the [d-Fe]/[d-Al] ratios reported by Buck et al. (2006, 2010b) and Shelley et al. (2018). The figures were described by Ocean Data View (Schlitzer, 2021).

Figures

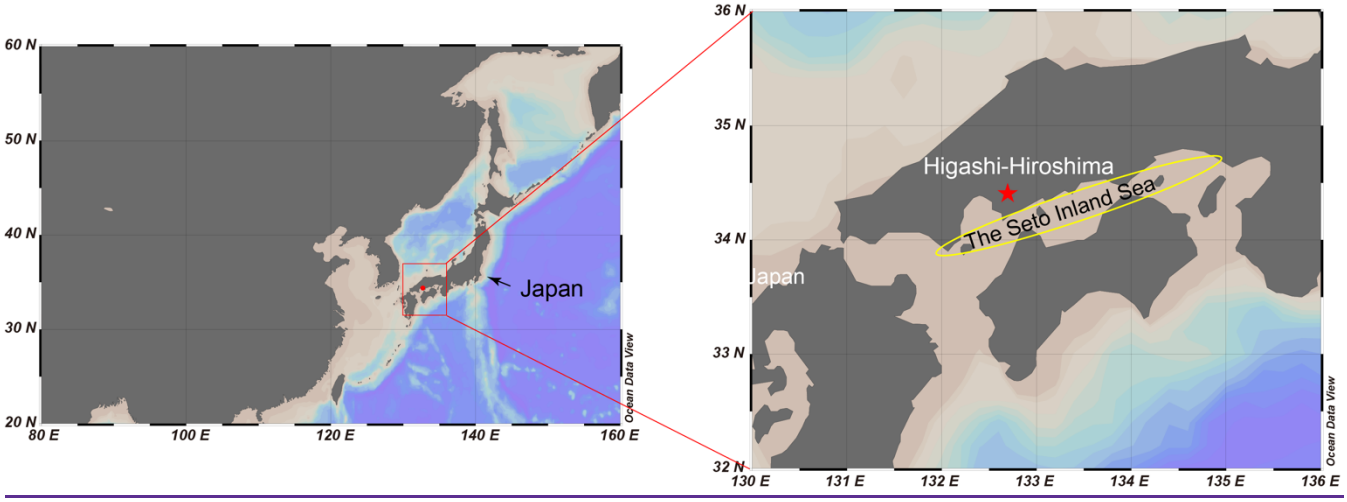


Figure 1: Sites (Higashi-Hiroshima) of size-fractionated aerosol sampling. Maps were visualized by Ocean Data View (Schlitzer, 2021).

~~Figure 6~~

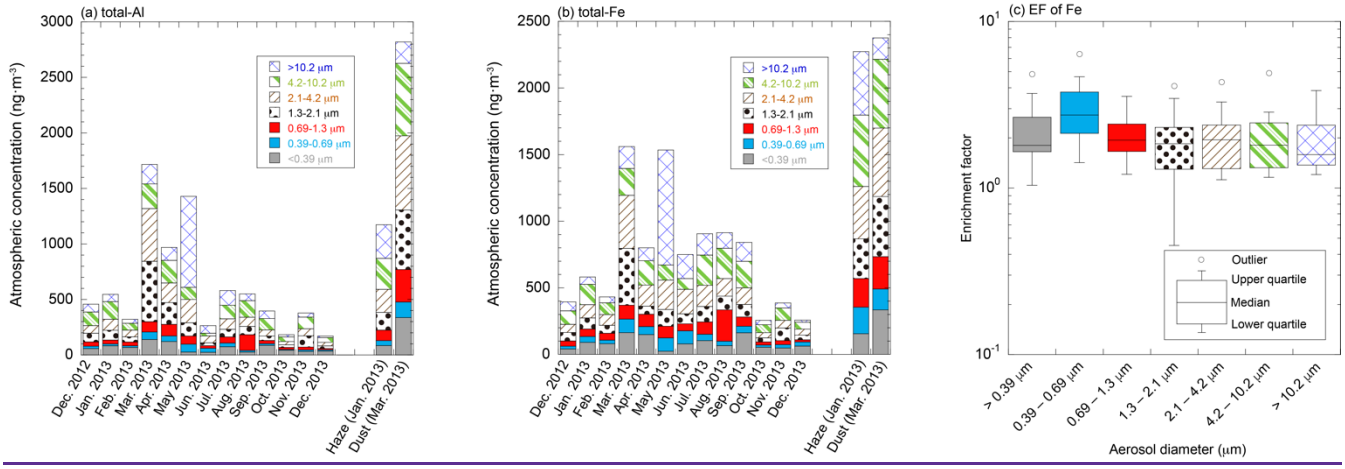


Figure 2: Monthly variations and size distributions of the (a) total Al and (b) total Fe concentrations. (c) Box plot of EF in each size fraction.

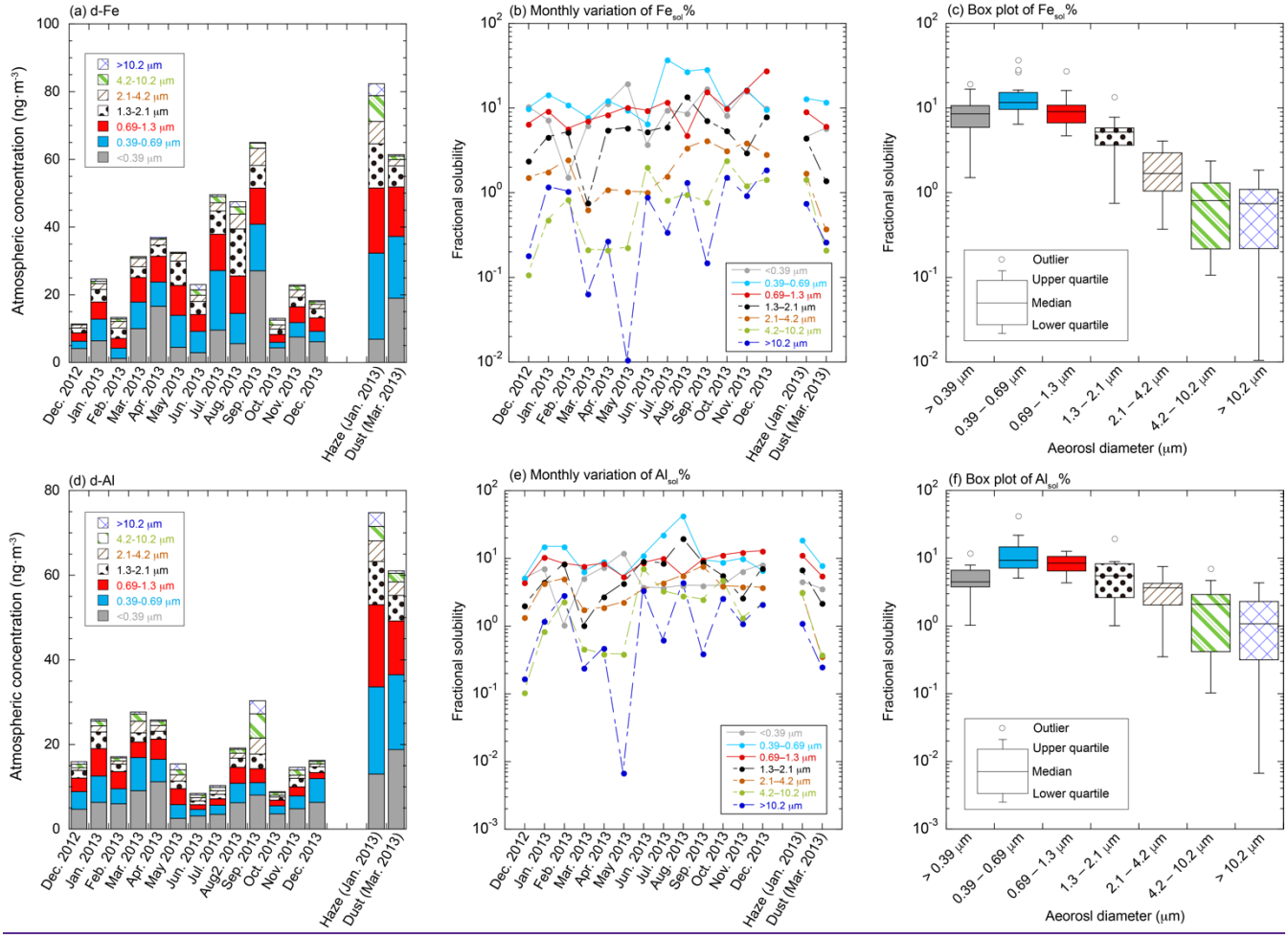


Figure 3: Monthly variation and size distributions of (a) d-Fe and (b) Fe_{sol}%. (c) Box plot of Fe_{sol}% in each size fraction. Monthly variation and size distributions of (d) d-Al and (e) Al_{sol}%. (f) Box plot of Al_{sol}% in each size fraction.

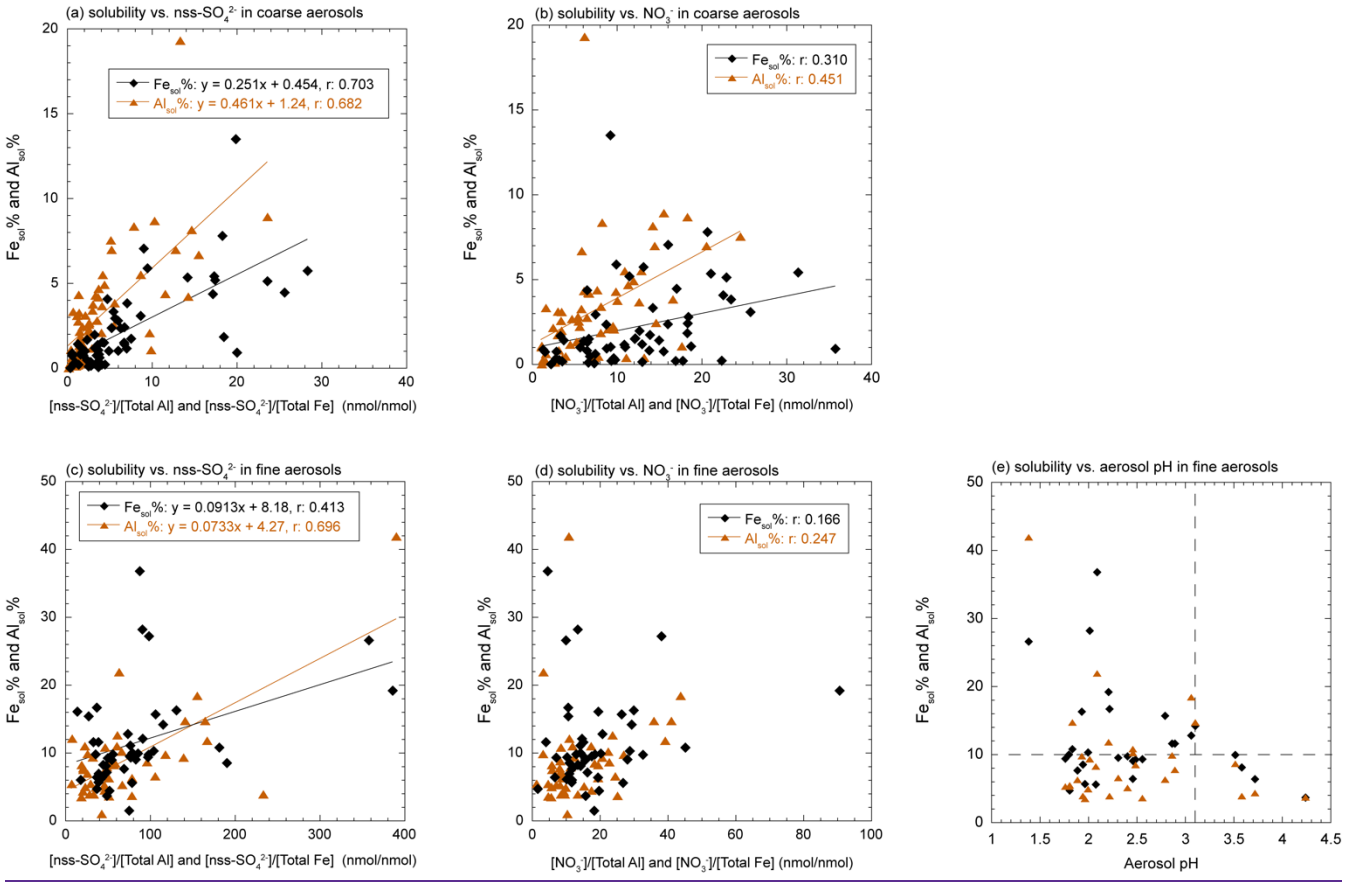


Figure ~~7~~4: Scatter plots of Fe_{sol}% and Al_{sol}% in coarse aerosol particles with (a) [nss-SO_4^{2-}~~/~~]/[total Fe~~ or~~] and [nss-SO_4^{2-}]/[total Al] and (b) [NO_3^-~~/~~]/[total Fe~~ or~~] and [NO_3^-]/[total Al~~,~~]. Scatter plots of Fe_{sol}% and Al_{sol}% in fine aerosol particles with (c) [nss-SO_4^{2-}~~/~~]/[total Fe~~ or~~] and [nss-SO_4^{2-}]/[total Al] , (d) [NO_3^-~~/~~]/[total Fe~~ or~~] and [NO_3^-]/[total Al~~,~~] and (e) aerosol pH.

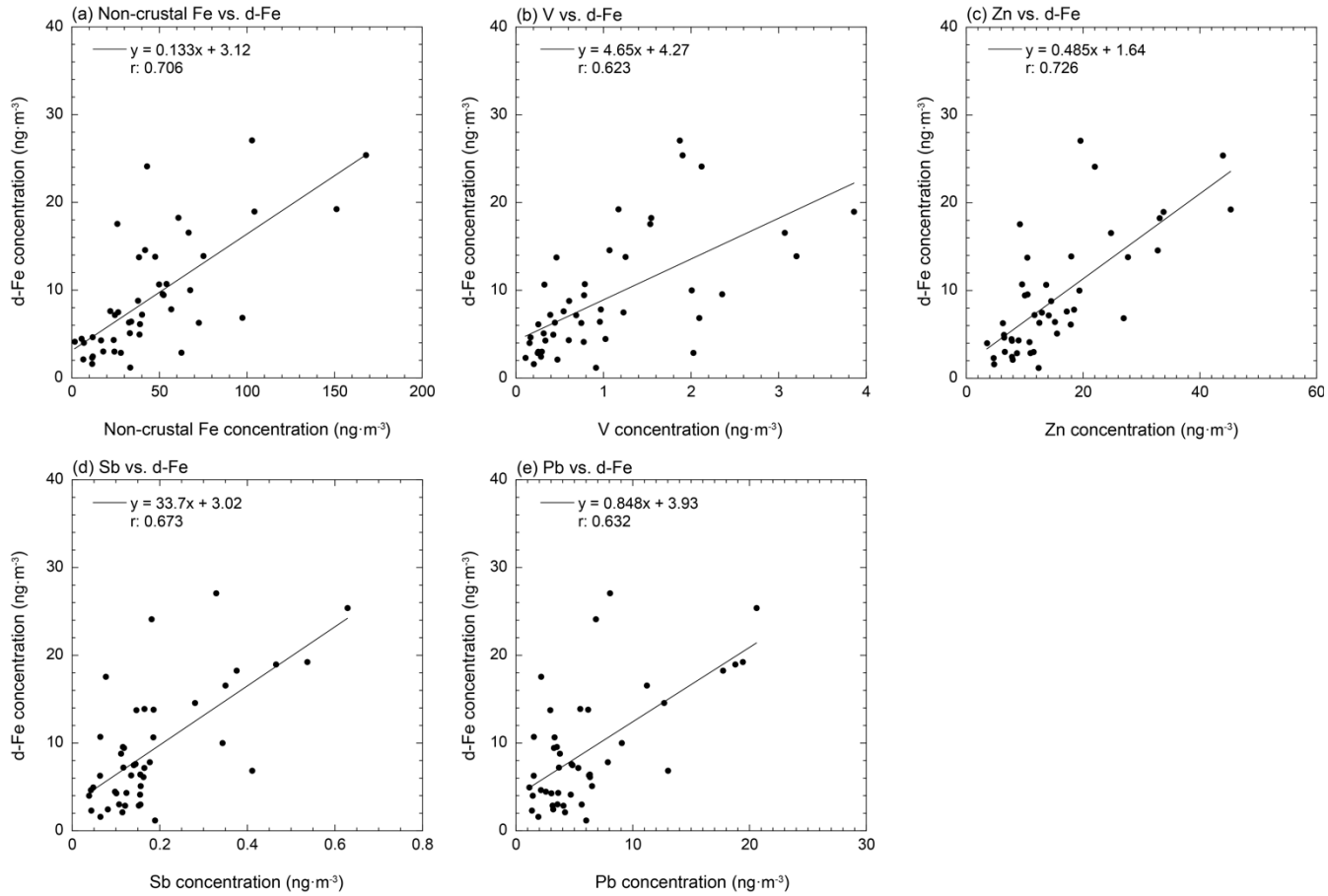


Figure ~~8~~5: Scatter plots of d-Fe with (a) non-crustal Fe, (b) total V, (c) total Cu, (d) total Sb, and (e) total Pb concentrations in fine aerosol particles.

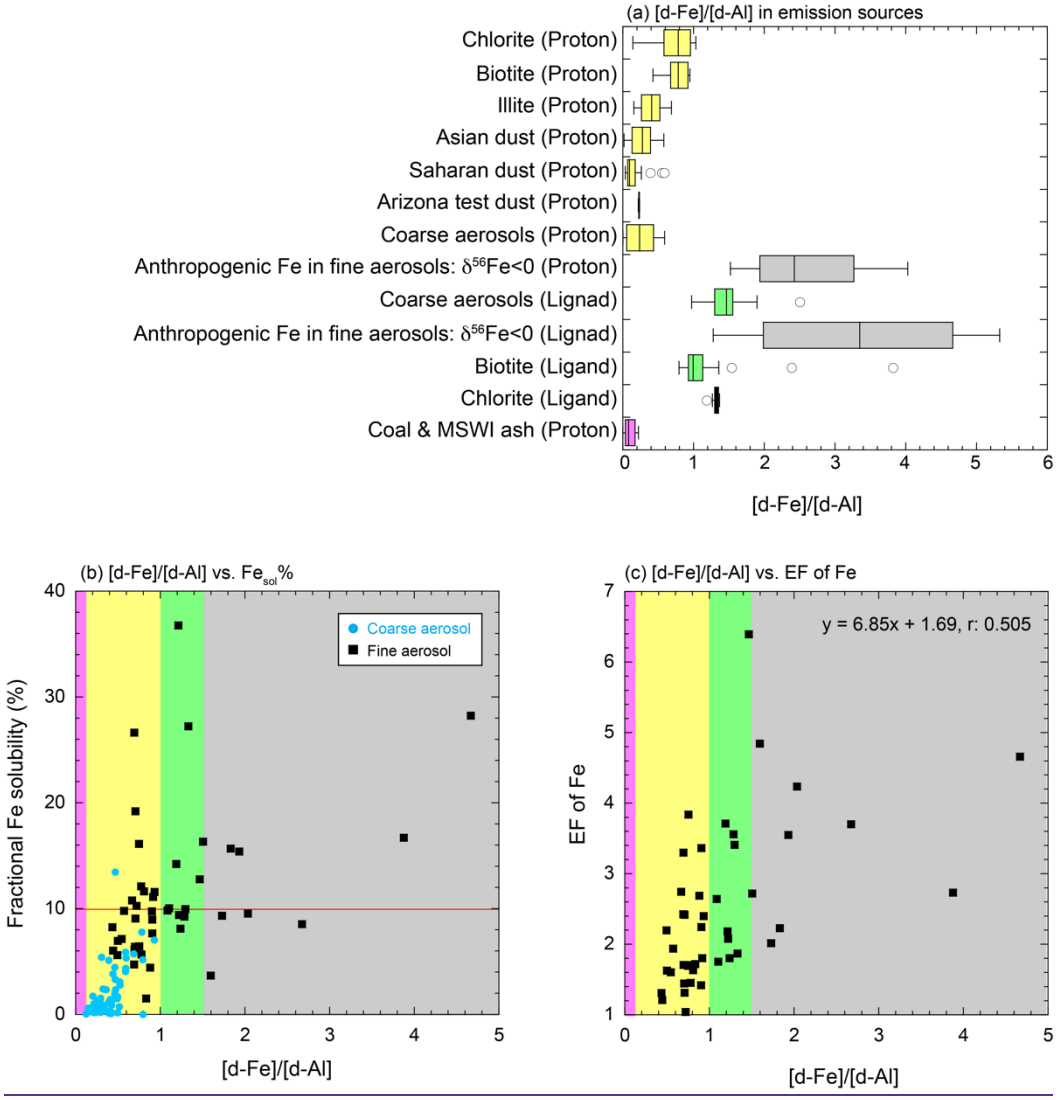


Figure ~~9~~6: (a) Box plot of [d-Fe]/[d-Al] in emission source samples ~~[P]~~(Proton) and ~~[L]~~(Ligand) indicating proton-~~promoted~~ and ligand-promoted dissolutions. Scatter plots of the [d-Fe]/[d-Al] ratio with (b) the Fe_{sol}% and (c) EF of Fe. Light blue circles and black squares in panels (b) and (c) represent the data on coarse and fine aerosol particles collected in Higashi-Hiroshima, respectively. Pink, yellow, light green, and gray regions show the typical ranges of the [d-Fe]/[d-Al] ratios of aluminosilicate glasses of coal combustion and MSWI, the proton- and ligand-promoted dissolution of mineral dust, and high-temp-FeOx, respectively. The regions were decided based on the ~~basis of the~~ box plots of panels (a).

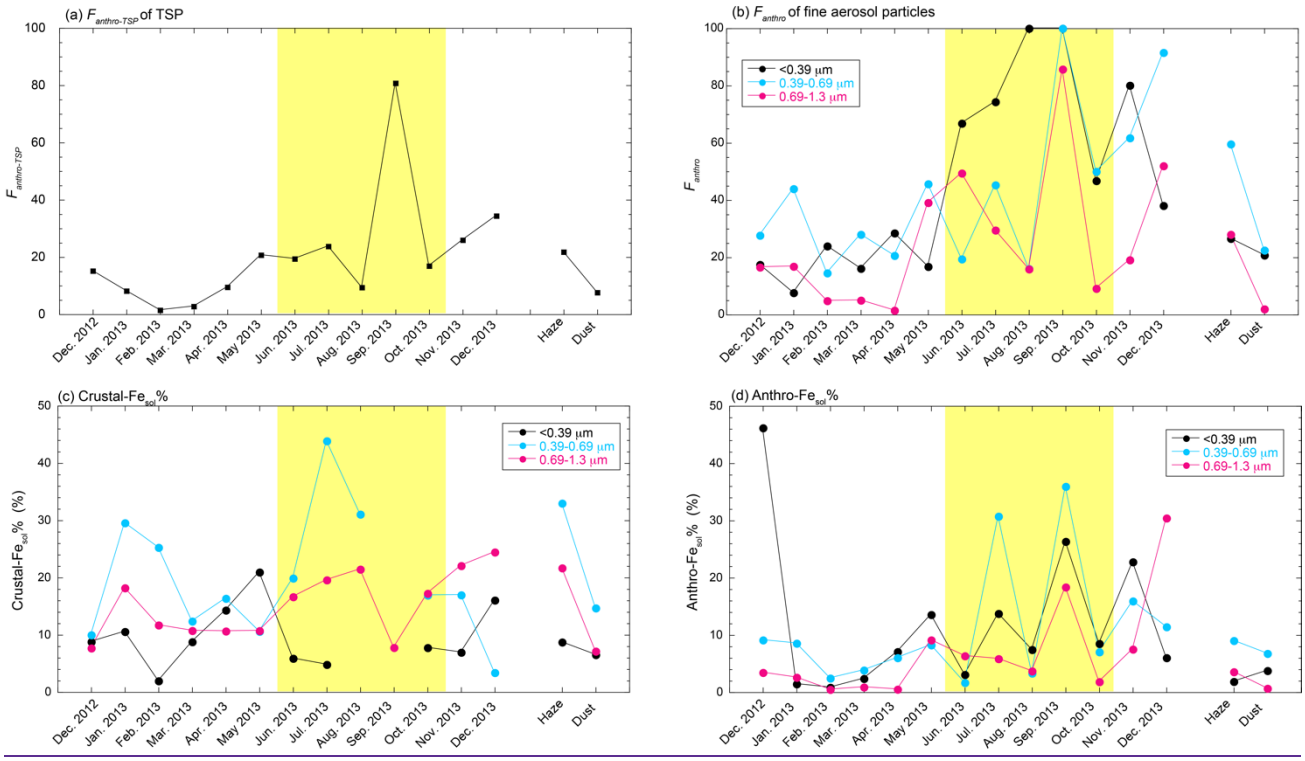


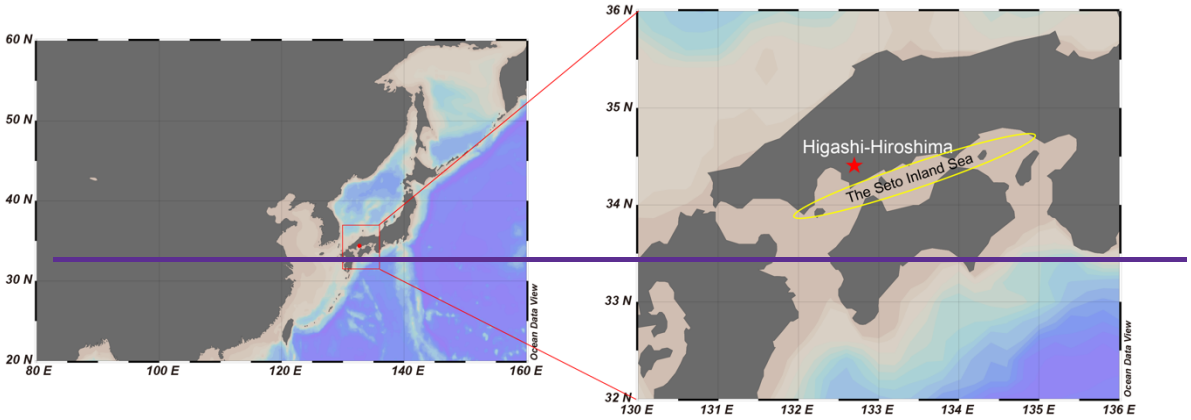
Figure ~~10~~7: Monthly variations of (a) non-crustal Fe fraction in TSP and (b) non-crustal Fe fraction in fine aerosol particles, (c) crustal-Fe_{sol}%, and (d) non-crustal Fe_{sol}% when the [d-Fe]/[d-Al] ratio of non-crustal Fe is 2.08.

~~Figure 11: Scatter plots of~~The yellow shaded region shows the ~~[d-Fe]/[d-Al] ratio with Fe_{sol}% in (a) TSP samples and (b) size-fractionated aerosol particles collected in the marine atmosphere. (c) The fraction of non-crustal d-Fe in these samples~~period when the air mass was ~~calculated by using Equations 6 and 7. The [d-Fe]/[d-Al] ratios of mineral dust in the Pacific and Atlantic Oceans were the average ratios of Asian dust (0.238) and Saharan dust (0.163), respectively. The [d-Fe]/[d-Al] ratio of non-crustal Fe was fixed at 2.08. The [d-Fe]/[d-Al] ratios of TSP and size-fractionated aerosol samples were adapted~~mainly derived from ~~Buck et al. (2006, 2010b), Shelley et al. (2018), Baker et al. (2020), and Sakata et al. (2022). The Fe isotopic ratio of TSP in the Atlantic Ocean was reported by Conway et al. (2019). Pink, yellow, light green, and gray regions in panels (a) and (b) show the typical [d-Fe]/[d-~~

Al] ratios of coal/MSWI fly ash, proton-promoted and ligand-promoted mineral dust dissolution, and pyrogenic Fe oxides, respectivelyJapan.

Figure 12: Non-crustal Fe fractions in TSP samples collected from (a) the Pacific Ocean and (b) Atlantic Ocean. Non-crustal Fe fractions were calculated by using reported [d-Fe]/[d-Al] ratios.

~~Figures~~



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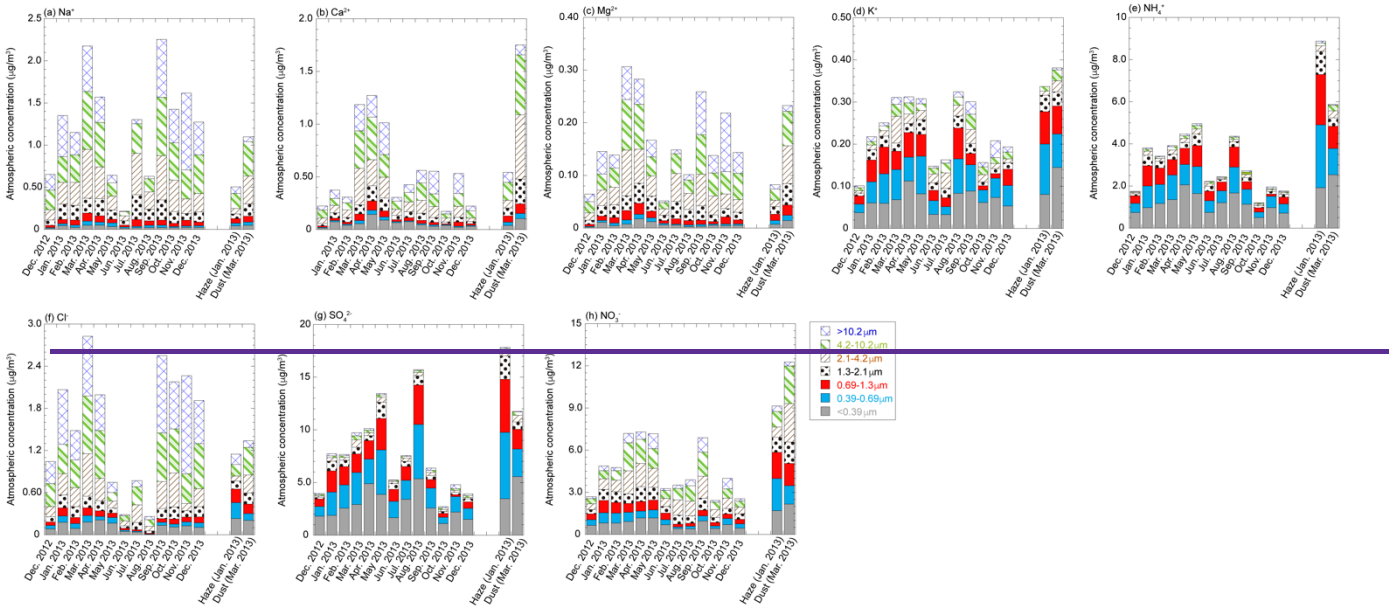

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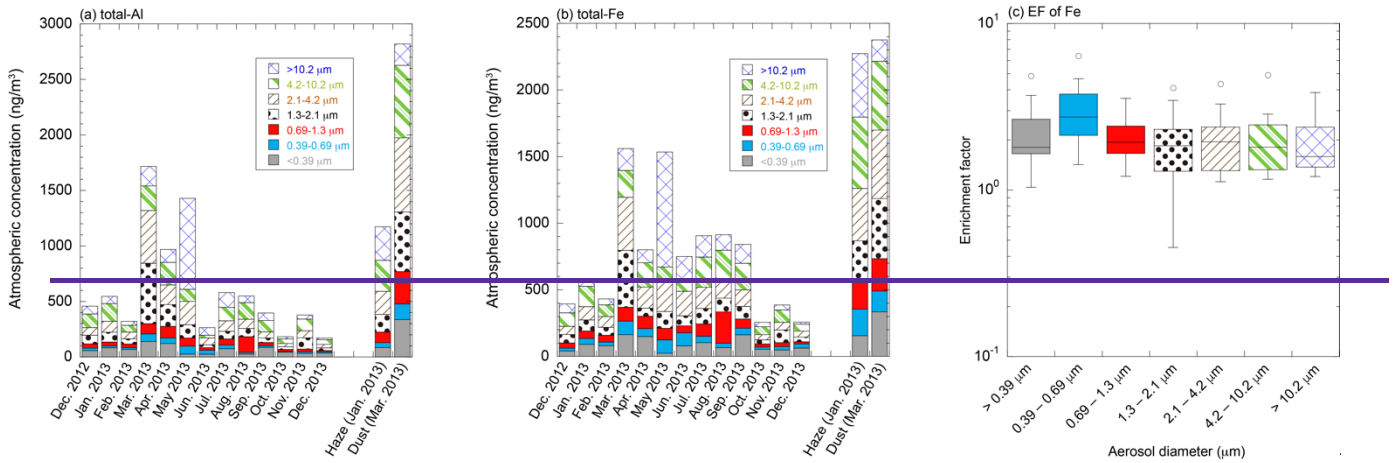

~~Figure 3: Monthly variations and size distributions of (a) total Al and (b) total Fe concentrations. (c) Box plot of Fe_{sol}% in each size fraction.~~

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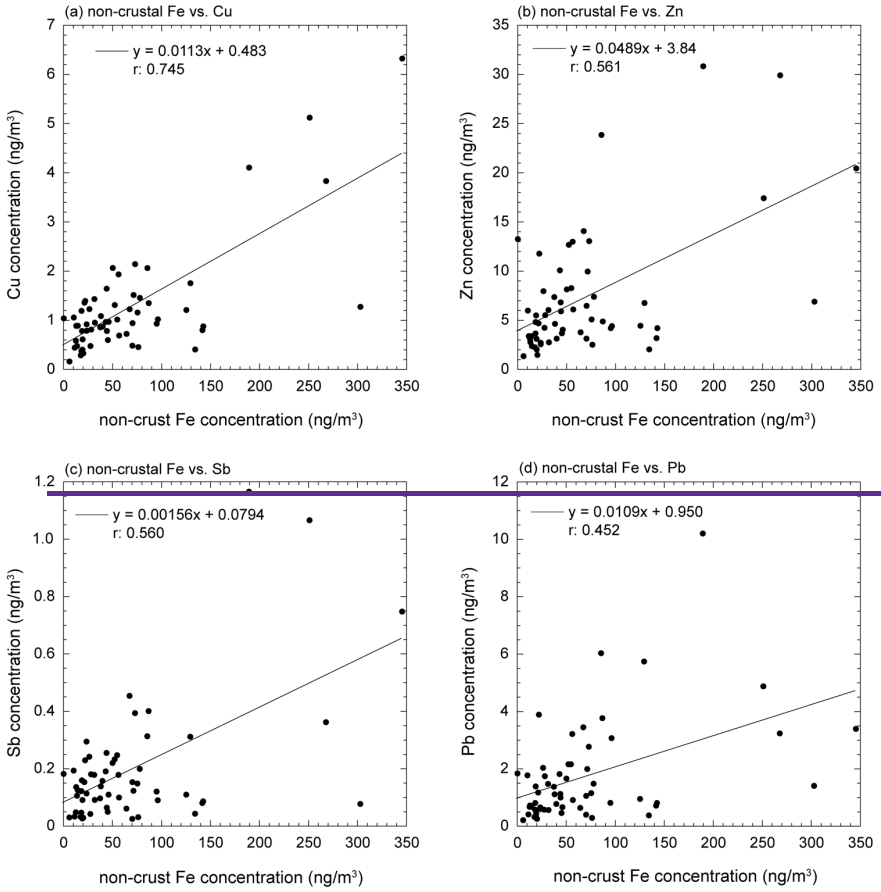


~~Figure 4: Scatter plots of non-crustal Fe concentration with (a) Cu, (b) Zn, (c) Sb, and (d) Pb in coarse aerosol particles.~~

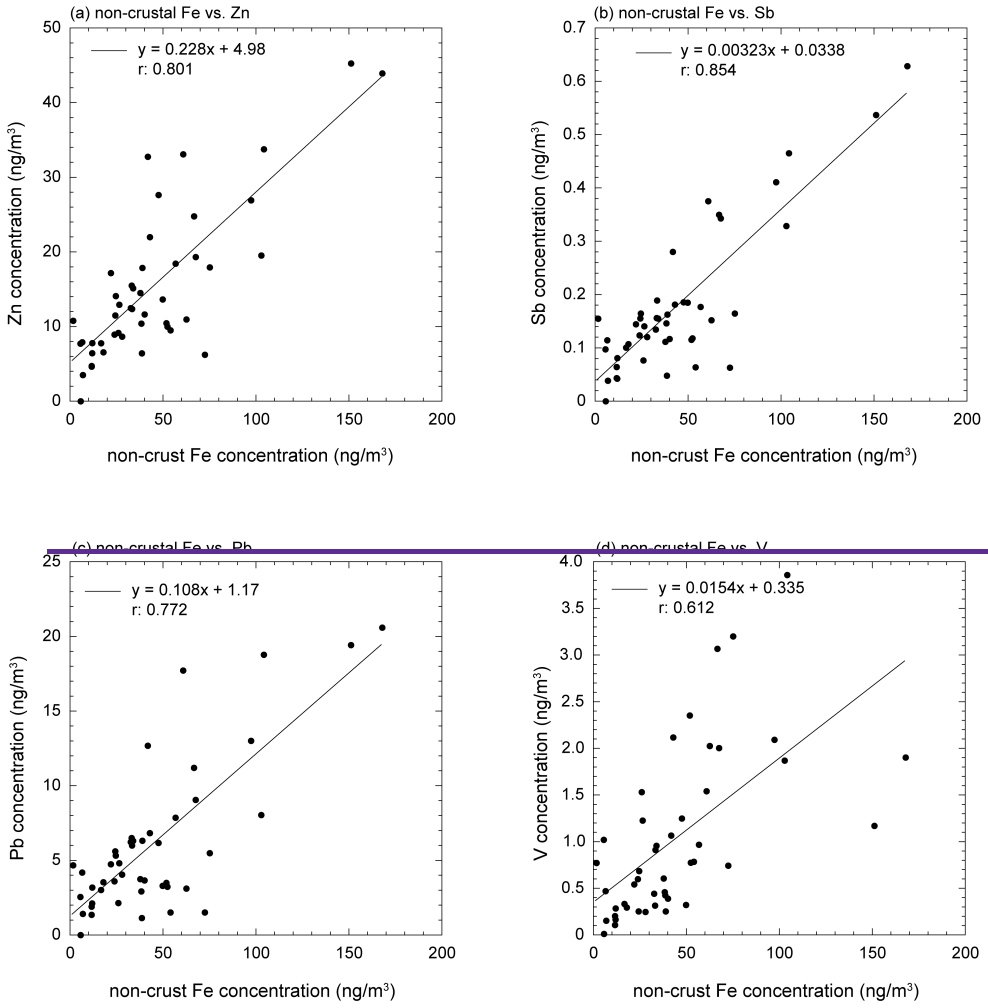
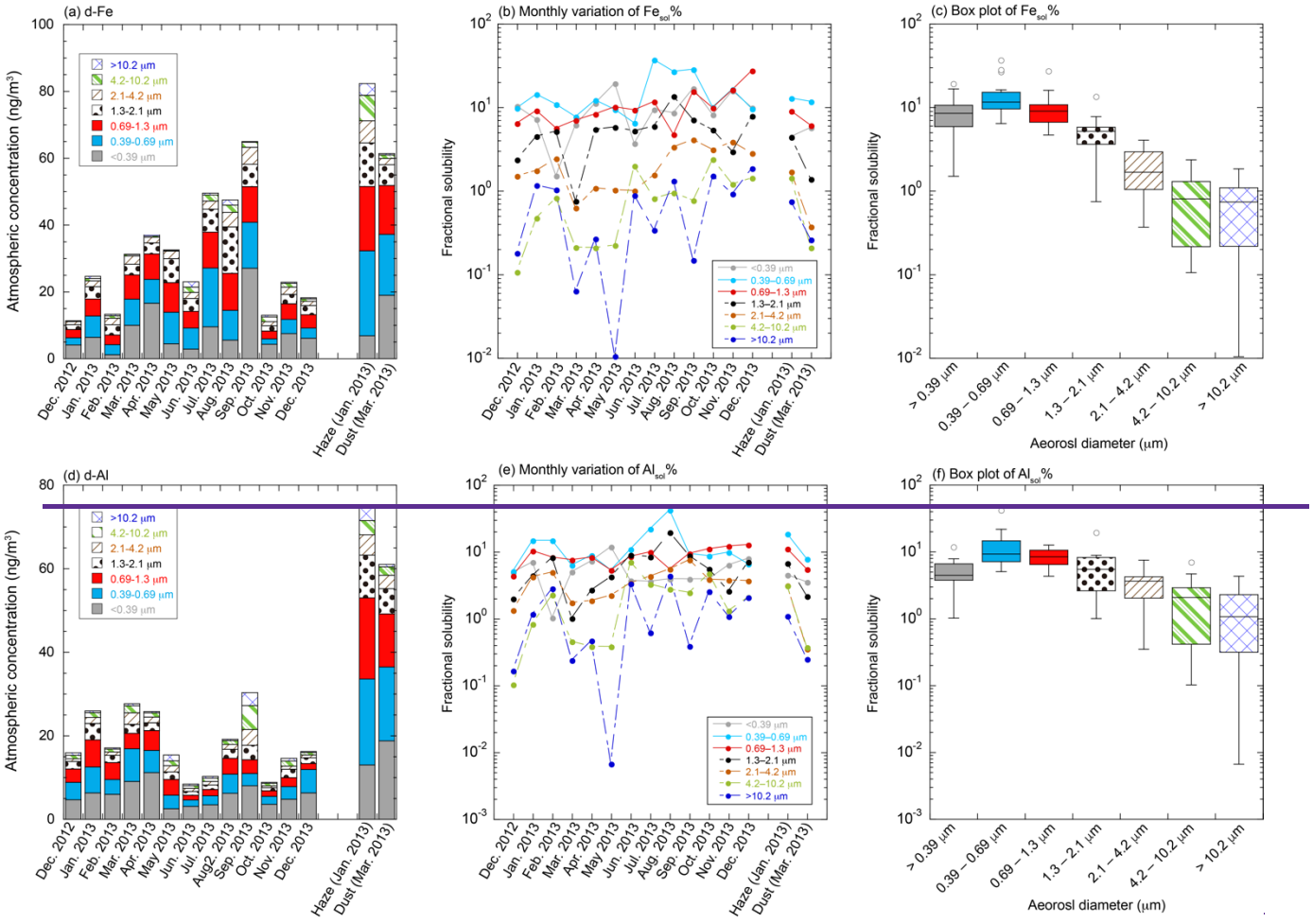


Figure 5: Scatter plots of non-crustal Fe concentration with (a) Zn, (b) Sb, (c) Pb, and (d) V in fine aerosol particles.



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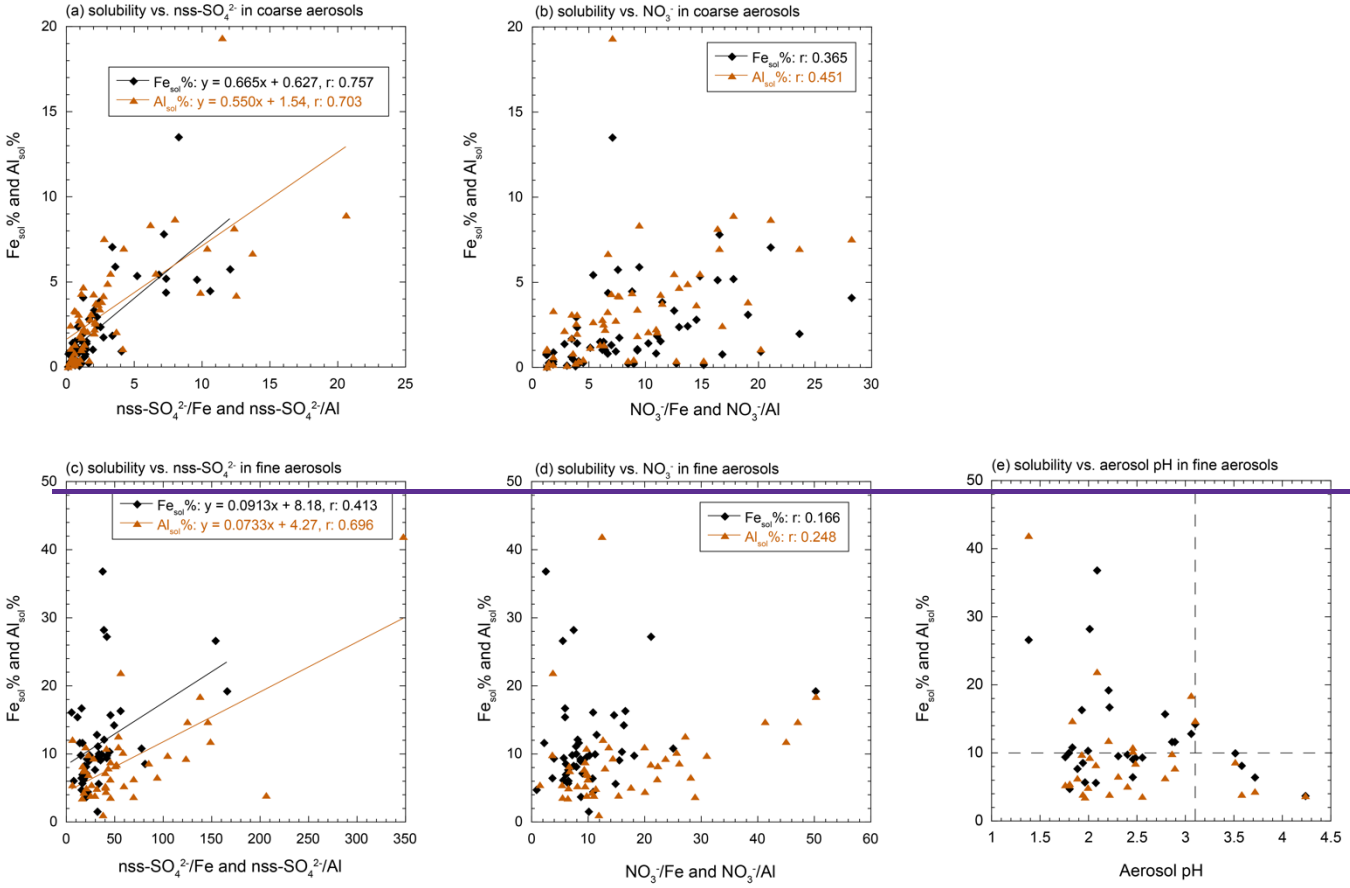

~~Figure 7: Scatter plots of Fe_{sol}% and Al_{sol}% in coarse aerosol particles with (a) nss SO_4^{2-}/Fe or Al and (b) NO_3^-/Fe or Al. Scatter plots of Fe_{sol}% and Al_{sol}% in fine aerosol particles with (c) nss SO_4^{2-}/Fe or Al, (d) NO_3^-/Fe or Al, and (e) aerosol pH.~~

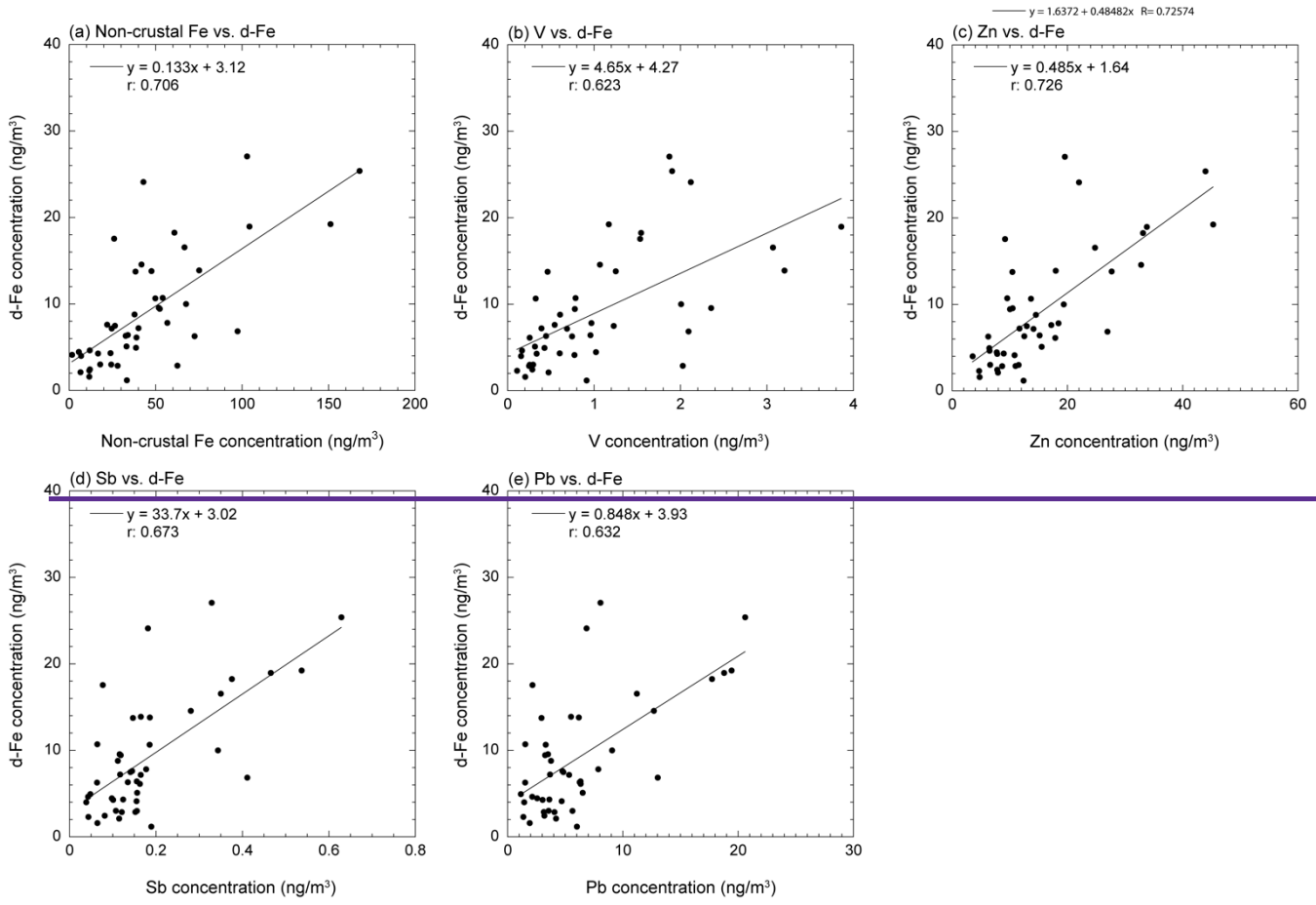

Figure 8: Scatter plots of d-Fe with (a) non-crustal Fe, (b) total V, (c) total Cu, (d) total Sb, and (e) total Pb concentrations in fine aerosol particles.

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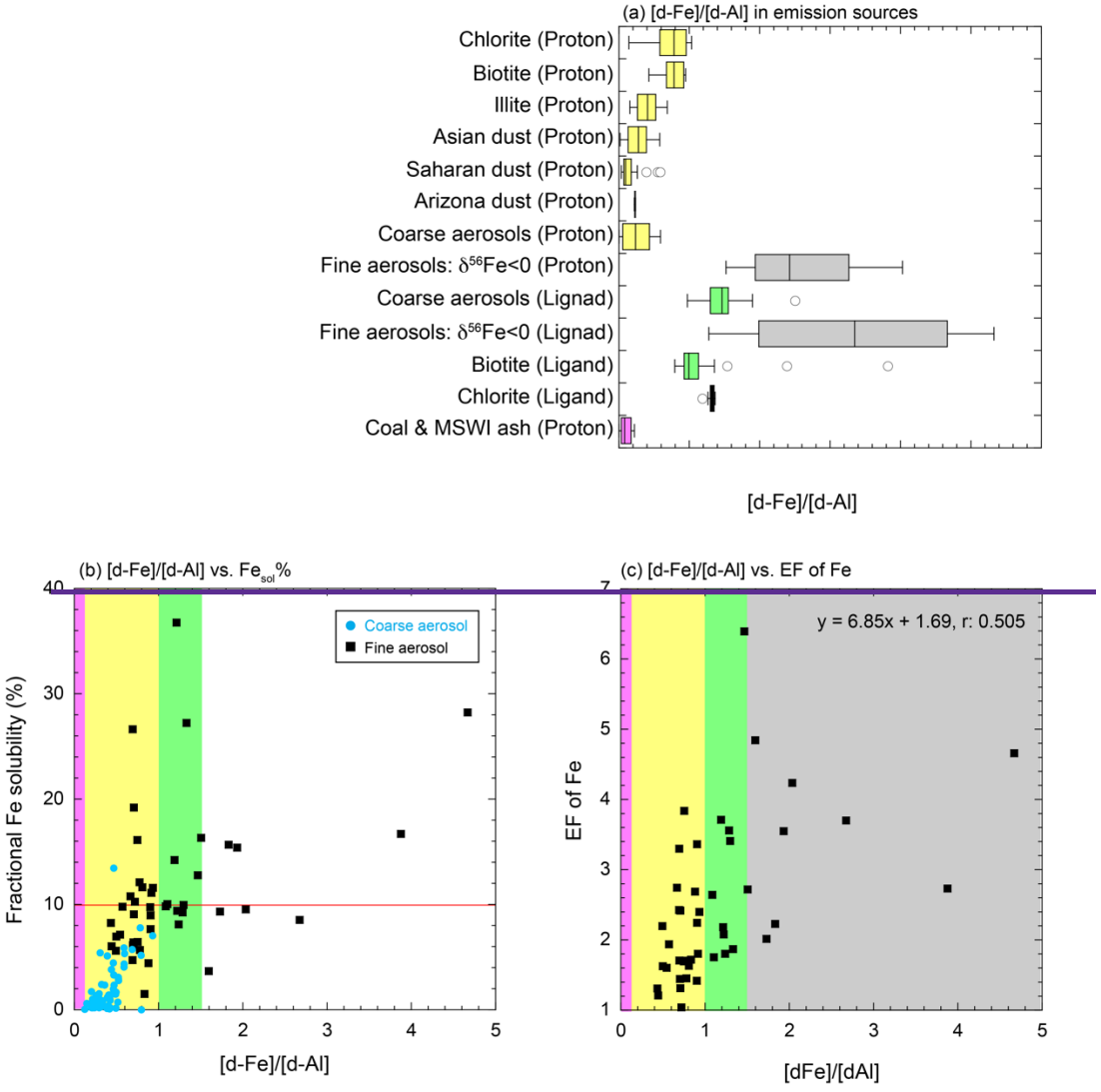


~~Figure 9: (a) Box plot of [d-Fe]/[d-Al] in emission source samples [P] and [L] indicating proton-promoted and ligand-promoted dissolutions. Scatter plots of~~

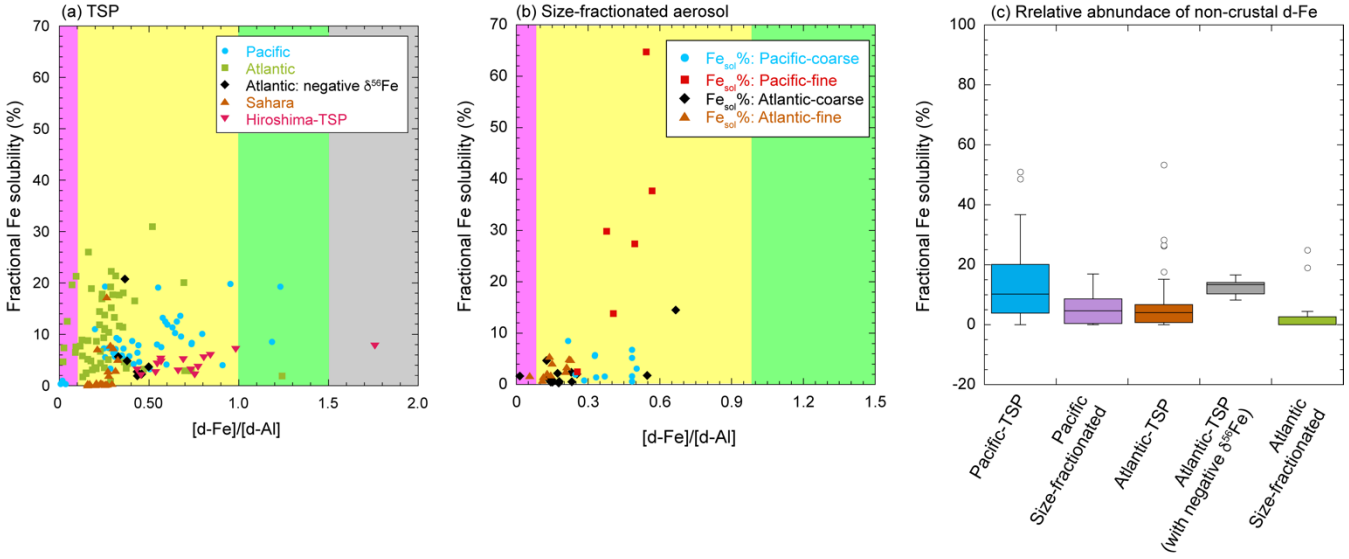
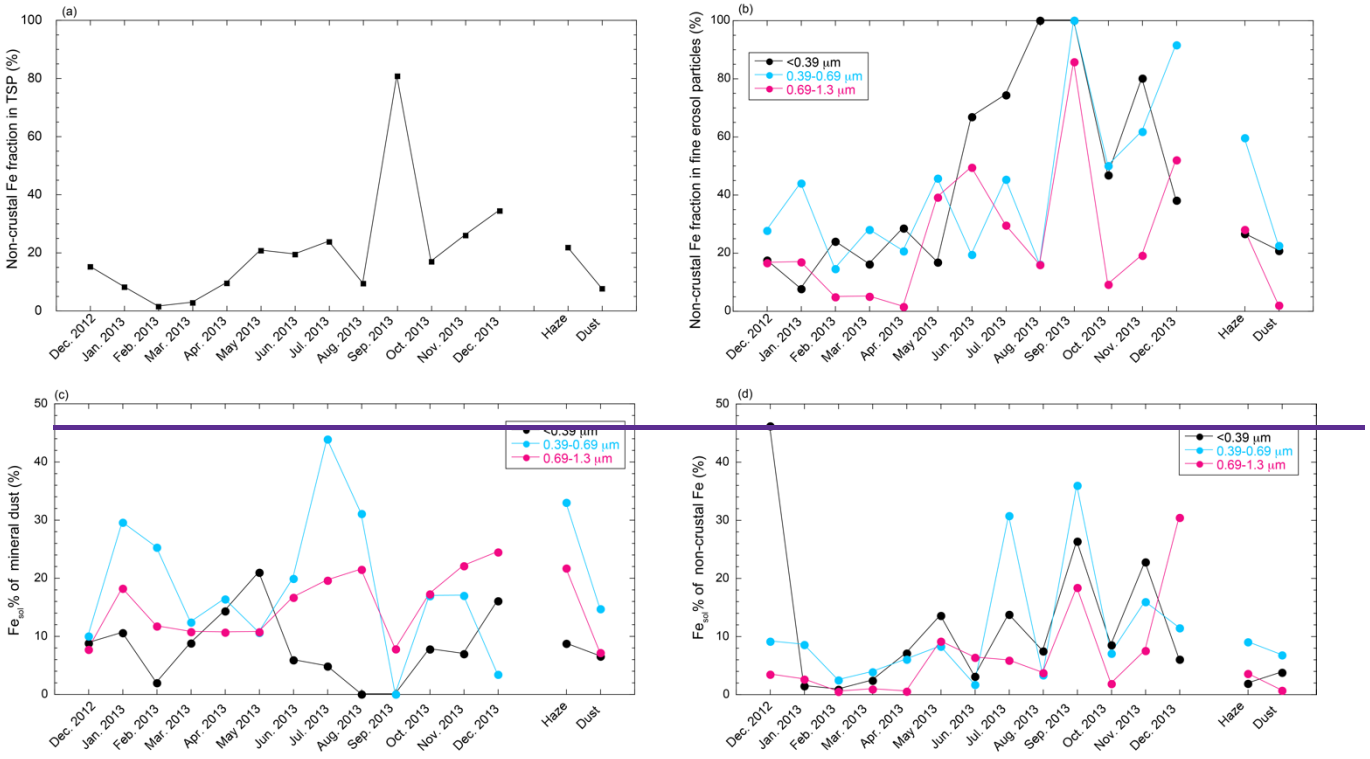
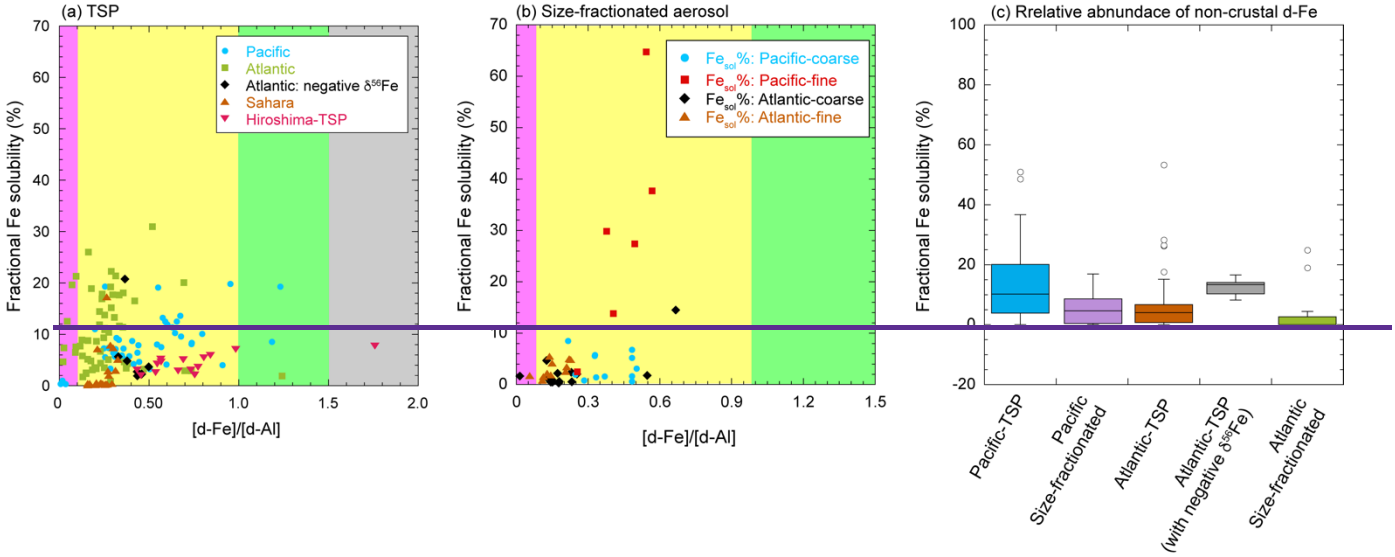


Figure 8 ~~[d-Fe]/[d-Al] ratio with (b) the Fe_{sol}% and (c) EF of Fe. Light blue circles and black squares in panels (b) and (c) represent the data on coarse and fine aerosol particles collected in Higashi-Hiroshima, respectively. Pink, yellow, light green, and gray regions show the typical ranges of the [d-Fe]/[d-Al] ratios of aluminosilicate glasses of coal combustion and MSWI, the proton- and ligand-promoted dissolution of mineral dust, and high-temp-FeOx, respectively. The regions were decided on the basis of the box plots of panels (a).~~



~~Figure 10: Monthly variations of (a) non-crustal Fe fraction in TSP and (b) non-crustal Fe fraction in fine aerosol particles, (c) crustal Fe_{sol}%, and (d) non-crustal Fe_{sol}% when the [d-Fe]/[d-Al] ratio of non-crustal Fe is 2.08.~~



~~Figure 11~~: Scatter plots of the [d-Fe]/[d-Al] ratio with Fe_{sol}% in (a) TSP samples and (b) size-fractionated aerosol particles collected in the marine atmosphere. (c) The fraction of non-crustal d-Fe in these samples was calculated ~~by~~ using Equations 6 and 7. The [d-Fe]/[d-Al] ratios of mineral dust in the Pacific and Atlantic Oceans were the average ratios of Asian ~~dust~~ (0.238) and Saharan ~~dust~~dusts (0.163), respectively. The [d-Fe]/[d-Al] ratio of non-crustal Fe was fixed at 2.08. The [d-Fe]/[d-Al] ratios of the TSP and size-fractionated aerosol samples were adapted from the works of Buck et al. (2006, 2010b), Shelley et al. (2018), Baker et al. (2020), and Sakata et al. (2022). The Fe isotopic ratio of TSP in the Atlantic Ocean was reported by Conway et al. (2019). Pink, yellow, light green, and gray regions in panels (a) and (b) show the typical [d-Fe]/[d-Al] ratios of coal/MSWI fly ash, proton-~~promoted~~ and ligand-promoted mineral dust ~~dissolution~~dissolutions, and pyrogenic Fe oxides, respectively.

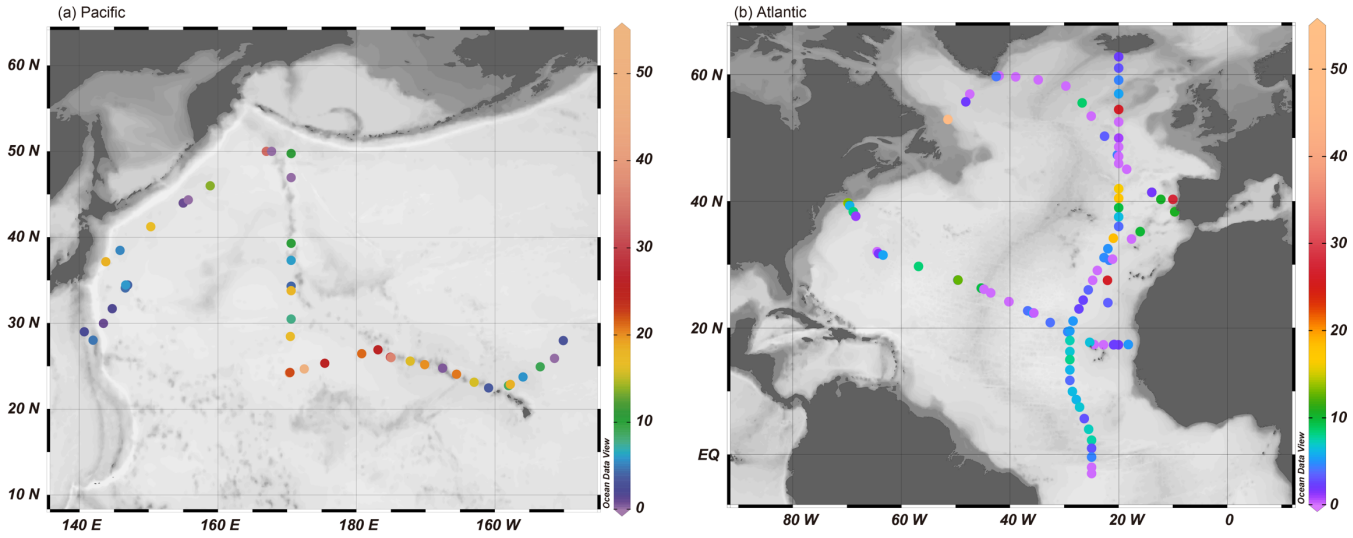


Figure ~~12~~9: Non-crustal Fe fractions in the TSP samples collected from (a) the Pacific Ocean and (b) Atlantic Ocean. Non-crustal Fe fractions were calculated ~~by~~ using ~~reported~~the [d-Fe]/[d-Al] ratios reported by Buck et al. (2006, 2010b) and Shelley et al. (2018). The figures were described by Ocean Data View (Schlitzer, 2021).

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