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Environmental Significance

Atmospheric aerosols effects on human and ecological health remain uncertain due to their highly complex and evolving nature. Global atmospheric and oceanic models need to incorporate more realistic representations of aerosol particles especially surface chemistry and physics. Accounting for the evolution in aerosol physicochemical properties due to redox reactions of transition metals, specifically Fe, is desirable as well. We highlight recent advances in our fundamental understanding of Fe reactivity in aerosols. Because of the complexity of Fe-containing aerosol particles from natural and anthropogenic sources, we call for the creation of transdisciplinary scientific networks to facilitate knowledge exchange and collaboration and efficiently improve predictive models whose results are used to advance knowledge and enact new policies.

A perspective on Iron (Fe) in the atmosphere: air quality, climate, and the ocean

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Abstract

As scientists engage in research motivated by climate change and the impacts of pollution on air, water, and human health, we increasingly recognize the need for the scientific community to improve communication and knowledge exchange across disciplines to address pressing and outstanding research questions holistically. Our professional paths have crossed because of our research activities that focus on the chemical reactivity of Fe-containing minerals in air, water, and at the air-sea interface. (Photo)chemical reactions driven by Fe can take place at the surface of the particles/droplets or within the condensed phase. The extent and rates of these reactions are influenced by water content and biogeochemical activity ubiquitous in these systems. One of these effects is the production of reactive oxygen species (ROS) that cause damage to respiratory organs. Another is that the reactivity of Fe and organics in aerosol particles alter surficial physicochemical properties that impact aerosol-radiation and aerosol-cloud interactions. Also, upon deposition, aerosol particles influence ocean biogeochemical processes because micronutrients such as Fe or toxic elements such as copper become bioavailable. We provide a perspective on these topics and

future research directions on the reactivity of Fe in atmospheric aerosol systems, from sources to short- and long-term impacts at the sinks with emphasis on needs to enhance the predictive power of atmospheric and ocean models.

1. Introduction

Connecting scientists studying key mechanistic aspects of mineral aerosols from source to sink is imperative in order to create a knowledge base that can be used in climate, oceans and health sciences. Often, the components of the research designed to elucidate the components involved in global biogeochemical cycling of Fe are performed separately from one another. For example, field campaigns for aerosol sampling studies characterize the concentration and particle-size distribution of the aerosols without advanced characterization such as morphology, phase, acidity, elemental mapping, and optical properties. Alternatively, laboratory experiments are conducted on simple materials that do not reflect the complex physicochemical processes of natural materials nor the physical processes that drive (photo)chemical transformations of their surfaces. Health impact studies may either be performed with samples that are not truly representative of actual aerosols or with the samples that are not fully characterized in terms of their surface functional groups. Large dust storms have high mass concentrations of particles in the coarse (diameter >1 μm) and accumulation (0.1 < diameter <1 μm) modes[1, 2], whereas dust particles from industrial emissions are mostly in the ultrafine mode (< 100 nm in diameter).[3-5] There is a growing concern in the public health community about the contribution of ultrafine particles to human health.[6] Because of their small size, these particles can cross the mucous membrane and circumvent the blood-brain barrier into the central nervous system causing disruption and potential death of nerve cells.[7] Coordination of research from molecular to global scales is desirable because molecular-level understanding of mechanisms that affect the physicochemical processes of atmospheric aerosol particles help in parametrizing Fe mobilization, aerosol direct and indirect effect on the global climate. For example, climate models generally do not capture well the complex surface chemistry of mineral aerosols.[8, 9] However, aerosol surface chemistry is critical in determining aerosol solution acidity, ionic strength, ligand-promoted, and organic acid-promoted photoreductive dissolution that ultimately affects the mobilization of Fe. The surface chemistry of real aerosol particles has not been studied extensively. Most detailed surface chemistry studies are done on synthetic particles rather than field-collected aerosols. Moreover, global models have difficulties in reproducing fine-scaled soil mineralogy, the chemical composition of Fe-laden anthropogenic aerosols, as well as their atmospheric transport and transformation, and removal.[8, 9] So, to improve the model parameterization of Fe at finer scales, nested global model or a combination of global and regional climate models can be explored.

Current atmospheric Fe biogeochemistry models consider mineralogy of dust and the chemical composition of combustion and biomass burning aerosols. These models also simulate the secondary formation of soluble Fe in the atmosphere.[10] However, most models consider bulk composition of the particle[11, 12] as including all details of aerosol chemistry and microphysics affecting Fe mobilization in global- and even regional-scale models is not practical. As the assumptions based on average properties and bulk chemistry are not likely to be highly accurate for simulating Fe mobilization in atmospheric aerosol, an alternative approach[10] would be to analyze detailed surface chemistry of airborne nanoparticles and link particle surface chemistry to soluble Fe formation, cloud condensation nuclei activity, radiative and health effects. The nanoparticles contained in the ultrafine fraction (< 100 nm) of these aerosols are often neglected because they are difficult to collect and analyze.[3] These nanoparticles will be the most chemically reactive because of extremely high surface areas and high concentrations of surface defects.[13]

Focusing on quantifying the presence, transport & transformation, and characterizing the bulk and surface properties of ultrafine fraction in aerosols will allow for parameterization based on the most important factors associated with a given process (e.g., interaction of UV, visible and IR radiation with mineral aerosol surfaces). This strategy requires collaboration among field, laboratory, and computational studies ranging from Global Climate Models to the nanoscale.

2. Atmospheric aerosol particles: from sources to impacts

In the lower troposphere, atmospheric aerosol particles originate from primary sources and secondary processes.[14-19] Primary aerosols include natural mineral dust, sea spray, terrestrial primary biological aerosol particles, primary organic aerosol, and anthropogenic dust such as fly ash from coal and fossil fuel combustion, and road dust. Gasoline- and diesel-powered motor vehicles, both on/off-road, are important sources of primary organic aerosols and precursors that drive secondary atmospheric reactions.[20] Secondary processes refer to particle formation from reactions in the atmosphere among gas phase inorganic and organic precursors leading to the formation of ammonium, non-sea salt sulfates, nitrates, and secondary organic aerosol, from ammonia, sulfur-containing gases, nitrogen oxides, and volatile organic compounds of biogenic and anthropogenic origins.[21-24] Also, secondary organic aerosol particles may form from condensed phase reactions during long range transport leading to particle growth.

The physical and chemical properties of aerosol particles are responsible for their effect on the energy balance of the atmosphere. Aerosols' ability to absorb and scatter solar radiation is referred to as the direct effect of aerosols on the climate. Their ability to influence cloud formation and lifetime and undergo chemical reactions via heterogeneous multiphase and bulk phase chemistry is referred to as the indirect effect on the climate. Aerosol properties also contribute to their toxicological effects and role in transmitting air-borne diseases such as COVID-19. During dust storm and smog events, aerosol particles reduce air quality and visibility. Inhaling fine particulate matter has been linked to diseases in the cardiovascular, respiratory, nervous and reproduction systems leading to cancers and premature deaths (see below section 3.2 on health impacts).[25] Upon deposition of aerosol particles, they may change the snow/ice surface albedo (because of their content of black carbon[26, 27] or hematite[28, 29]) and ocean biogeochemical processes (because of their content of micronutrients such as Fe).[30] Hence, research in atmospheric aerosol chemistry involves investigating changes to the chemical and physical properties of aerosols during their residence time in the atmosphere (*aerosol aging*) and secondary pathways that lead to new particle formation and growth. Terrestrial sources and atmospheric aging also influence the amount of Fe that can be mobilized and become accessible for aquatic life after the deposition of aerosols to the surface ocean. Characterization of bioaccessibility of atmospheric Fe remains one of the priorities for improved representation of the global carbon cycle and climate.[31]

Once emitted, aerosol particles undergo acid processing under variable amounts of adsorbed water which impacts their hygroscopic properties and chemical reactivity. These processes take place at the surface of the particles/droplets or within the condensed phase. The surface-to-volume ratio of atmospheric aerosols determines the dominance of surface versus bulk reactions in changing the chemical composition and physical properties of the particles. There is great interest in quantifying the acidity of atmospheric water in wet aerosols, cloud droplets, precipitation, and fog droplets.[32] In general, wet aerosols are highly acidic ($pH < 2$) compared to droplets in clouds, precipitation and fog (pH 2-5) mainly due to differences in the proton activity calculated from the amounts of ammonia/ammonium, sulfuric/nitric acids, organic acids and liquid water content.[32] The highly acidic water content in aerosol particles can catalyze a number of chemical processes such as solubilization of metal oxides, and formation of secondary organic and inorganic components aerosols.[33] Variation in temperature and relative humidity results in cycling between wet aerosols with adsorbed water and liquid droplets, and that has consequences on the size, solute:solvent ratio, surface composition, acidity, ionic strength, and phase, with impacts on the overall particle reactivity and mineral solubility. Also, the importance of heterogeneous reactions at the gas/liquid interface increases with decreasing particle size.[34] These reactions are also relevant to the surfaces of oceans and lakes. Samples used in laboratory studies for probing chemistry at the gas/liquid interface are either thin water/solution films on substrates, microdroplets, or simply a beaker/petri dish with liquid. There are molecular-level differences in water structure at the gas/water interface versus the bulk. These differences affect rates and mechanisms of interfacial (photo)chemical reactions.[35, 36] For example, Chapleski Jr. *et al.*[37] reviewed heterogenous reactions of ozone with organic surfaces and reported that chemistry of aqueous microdroplets of phenol, α-tocopherol, β-caryophyllene and highlighted differences in ozonolysis reaction products between air-water shell and bulk solution. The differences in reactivity were due to water density changes and the rate of vibrational relaxation changes, which allows for activation of mechanistic pathways that lead to different products. Lee *et al.* showed that chemistry in 1-50 μm aqueous microdroplets induce spontaneous reduction of organics[38] and generation of hydrogen peroxide[39] due to molecular differences in water structure in confined micro-scale space that renders water molecules electrochemically active without adding electron donors or acceptors. Tahara and co-workers [40] used surface specific ultra-fast vibrational sum frequency generation to study the photochemical dissociation of phenol to a hydrated electron and a hydronium ion through an electronically excited state at the air-water interface, and found that the photoionization reaction of phenol proceeds 10^4 times faster at the water surface than in the bulk aqueous phase (upon irradiation with photons with the same energy). As reviewed by Zhong *et al.*[36], molecular dynamic simulations of reactions at the aerosol water surface confine the atmospheric species into a specific orientation. The hydrophilicity of these atmospheric species, or the hydrogen-bonding interactions between them and interfacial water, explain this observation.

Moreover, aging of aerosol particles changes their mixing state and morphology as shown in Fig. 1 per You *et al.*[41], Li *et al.*[42] and Song *et al.*.[43] These classifications highlight spatial distribution of elements and organic species include composition as well as they are based on measurements from single particle techniques in a population of aerosol as reviewed in Riemer *et al.*[44] and Laskin *et al.*[45] These techniques include electron and atomic force microscopy, vibrational spectroscopy and mass spectrometry. For example, transmission electron microscopy images coupled with elemental analysis reported by Xu *et al.*[46] showed three aerosol morphologies from field campaigns designed to trace the movement of an Asian dust storm over continental and marine areas. They reported changes to soot morphology from chain-like morphology in the fresh aerosol population to partially embedded soot due to continental aging. Upon marine aging, the soot population was described as fully embedded. In another example by Lee *et al.*[47], scanning electron microscopy data revealed six key morphologies of sea spray aerosol where prism-like, core–shell, and rounded morphologies accounted for more than 99% of the entire sea spray aerosol population and the distribution of the particles over the morphologies exhibited size-dependent trends. Also, a significant increase in the organic mass fraction of sea spray aerosol was observed with decreasing particle size.

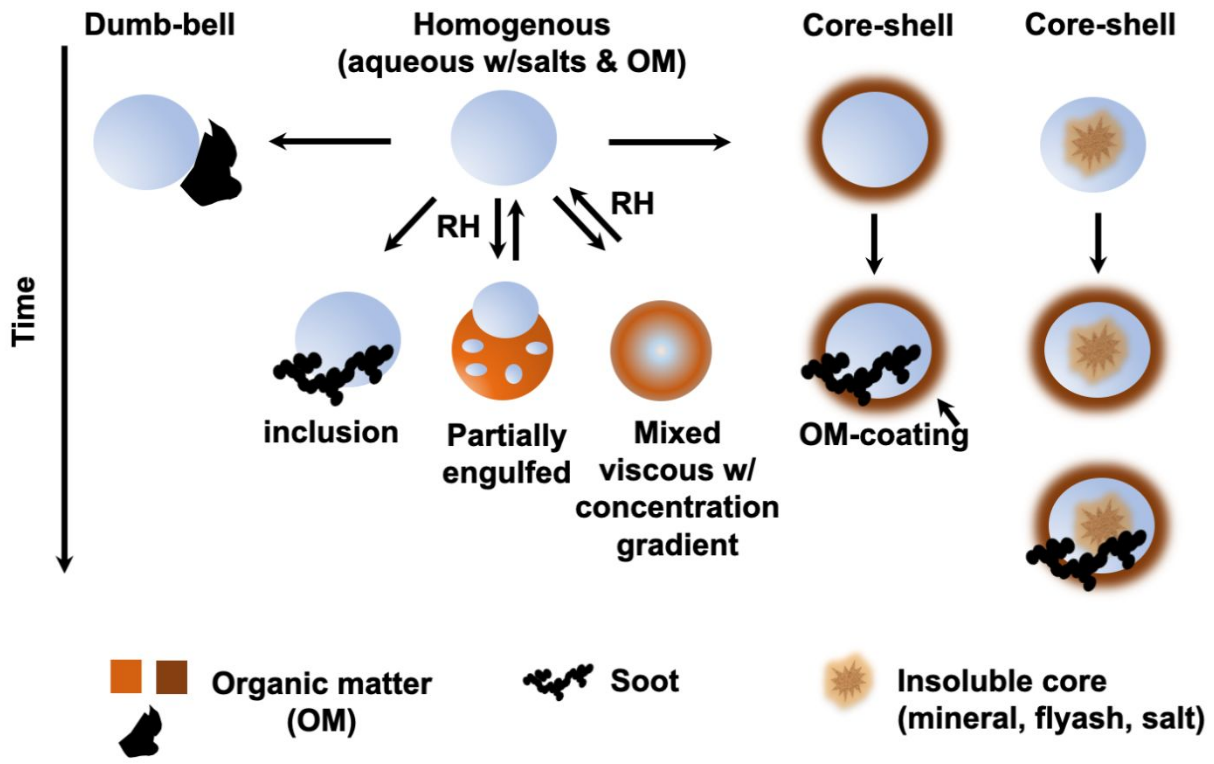

Fig. 1 Schematic of major atmospheric aerosol morphology and mixing states per You *et al.*[41], Li *et al*.[42] and Song *et al.*[43] as they change with time and composition. From left to right: (top panel) dumb-bell, homogeneous aqueous with salts and organic matter (OM), and core-shell. (middle panel) inclusion, partially engulfed, mixed viscous with concentration gradient, and OM-coating. Adapted with permission ref. [48] under the Creative Commons BY-NC license. © 2021 The Author(s).

Organic carbon makes up a large percentage of the aerosol mass in general. One of the active areas of research in atmospheric chemistry is related to the optical properties of organic carbon because they are related to the direct effect of aerosols. Optical properties range from colorless for low molecular weight hydrocarbons and derivatives all the away to black carbon, which has radiative forcing second only to that of CO_2. In between these two extremes, there is a class of organic carbon called 'brown carbon' referring to light-absorbing organic compounds in atmospheric particles that include polycyclic aromatics, humic-like substances, biopolymers, etc. Interactions of organic matter with metal oxides and minerals occur via a number of mechanisms depending on their functional groups that include chelation, ligand exchange, electrostatic, van der

Waals and hydrophobic interactions, cation bridging and hydrogen bonding. These processes lead to changes in surface charge and functional groups, hydrophobicity, interfacial water structure, adhesion strength, and dissolution of the oxide/mineral phase such as Fe-(oxyhydr)oxides.

In their review of the phase of organic particles, Reid *et al.*[49] provided a comprehensive synthesis of the literature of field observations and laboratory studies on the viscosity ranges of secondary organic aerosol particles since it is challenging to directly measure particle viscosity. While the viscosity of secondary organic aerosol particles has been assumed to be liquid in gas-particle partitioning models, experimental evidence using a variety of techniques showed that they could be in semi-solid or solid states under ambient conditions.[49] In the presence of hygroscopic salts, variation in relative humidity affects the amount of aerosol liquid water leading to phase transitions (deliquescence with increasing relative humidity and efflorescence with decreasing relative humidity). In multicomponent aerosol system containing salts and organics, liquid-liquid phase separation takes place over a different relative humidity range than pure systems[43], and the process is also pH-dependent.[50, 51] The above section highlights the complexity in the chemical composition and processes in mineral dust and organic aerosol which undergo mixing in the atmosphere. Therefore, establishing connections among the research groups that focus on each type of atmospheric particles would result in a holistic understanding to their reactivity and its impact on physicochemical properties in a timely fashion. The following section focuses on Fe as the most abundant transition metal in mineral dust aerosol to highlight its role in changing aerosol physicochemical properties.

3. Metals in atmospheric aerosol particles: the case of Fe from sources to impact

A major source of Fe-containing aerosols is mineral dust with estimated emissions of 2000 Tg per year.[52] Mineral dust has the highest atmospheric loading compared to the other types of aerosols that include sea spray, sulfate, black and organic carbon. Fe_2O_3 is the third most abundant oxide component after alumina and silica by mass in the Earth's crust, the source of mineral dust aerosols. Combustion sources are increasingly being recognized as important contributors to labile Fe deposited on the oceans.[53] A number of operational terms are used to describe Fe species in deliquesced aerosol solution, cloud/rainwater, and seawater. Here, we adopt the suggested definitions by Meskhidze *et al.*[31], which include particulate (PFe), colloidal (CFe), dissolved (DFe), and soluble (SFe) referring to Fe species that are retained by 0.2 μm membrane filters, retained by 0.02 μm membrane filters, pass through 0.2 μm membrane filters, and pass through 0.02 μm membrane filters, respectively. The typical SFe concentration in cloud droplets (dia. 20 μm size) is 1 μM and can reach up to 10^3 μM depending on the location.[54] Quantifying SFe concentration in an aerosol particle (dia. 0.2 μm size) with aerosol liquid water is problematic due to the variability in the amount of aerosol liquid water , which is temperature- and relative humidity-dependent. When cloud droplets evaporate, SFe concentration can be estimated to be as high as a 10^3 mM due to droplet size reduction. Another way of estimating SFe in fine particles was reported earlier[55], where amount of aerosol liquid water (6×10^{-8} L m^{-3}) was estimated from a thermodynamic model and used with Fe solubility (i.e., total dissolvable iron solid iron oxides in a sufficiently acidic solution, 5%) and typical levels of Fe in solid fine particles from across China (331-1640 ng m^{-3}). When these aerosol parameters are used, Fe concentrations would range from 5–24 mM. This large change in the concentration of SFe with size will impact the rates of chemical reactions involving Fe as a reactant or catalyst.

As a redox- and photo-active element capable of forming relatively strong complexes with inorganic and organic compounds, Fe species are reactive over a wide range of solubility and reaction conditions of environmental relevance. Processing of Fe-containing particles takes place in the atmosphere through reactions with acidic gases, organics, in the dark or under irradiation, which changes the hygroscopicity of these particles and hence amount of dissolved Fe (Fig. 2).

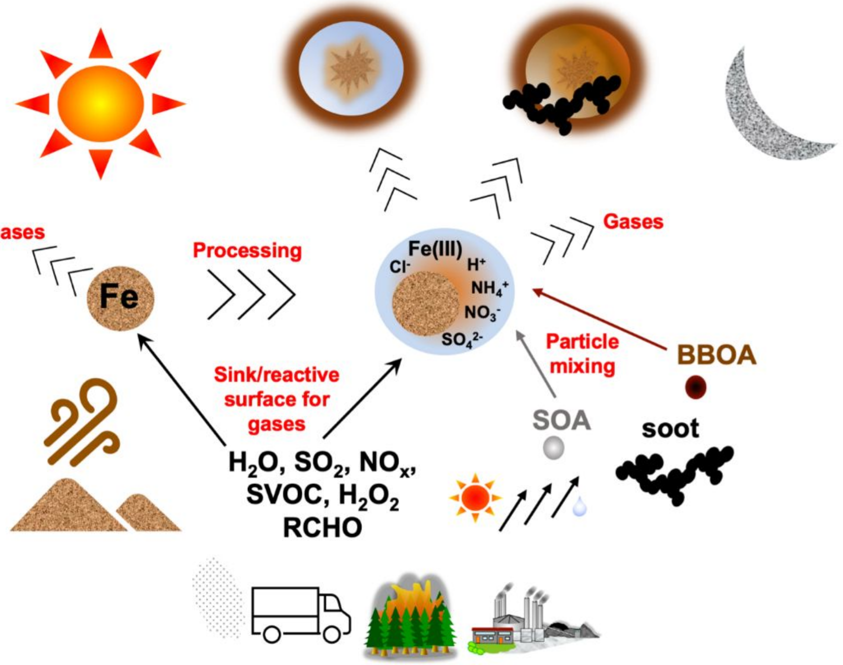

Fig. 2: Illustration of the atmospheric aging of Fe-containing particles that changes their physicochemical properties during their residence time. Gas phase contains water (H_2O), sulfur dioxide (SO_2), nitrogen oxides (NO_x), semi-volatile organic compounds (SVOC), hydrogen peroxide (H_2O_2), and aldehydes (RCHO). Examples of organic aerosols are secondary organic aerosols (SOA) and biomass burning organic aerosols (BBOA). The deliquesced and aged Fe aerosol particles contain other chemicals such as chloride (Cl^-), protons (H^+), ammonium (NH_4^+), nitrate (NO_3^-), and sulfate (SO_4^{2-}).

The processed Fe-containing particles can act as a sink for inorganic, volatile and semi-volatile organic compounds from combustion and biomass burning. They can also undergo mixing with secondary organic aerosol, soot, and biomass burning organic aerosol. Changes to particle size, phase, morphology, optical properties, and chemical composition could take place with aging time.

Also, new gas phase species due to condensed and heterogeneous multiphase chemistry could also be released. Hence, the reactivity of soluble and insoluble Fe in the fresh and processed particles would have impacts on health, climate, and ocean biogeochemistry as detailed in the following sections.

3.1 Air quality and health impacts

Pollutants used as indicators for air quality include nitrogen oxides, ozone and fine particulate matter ($PM_{2.5}$ and PM_1) from natural and fossil fuel combustion sources, which contain transition metals such as Fe.[56] These pollutants are used in calculating the air quality health index. Some PM forms in the atmosphere from reactions of volatile organic compounds.[57] The combination of climate change and air pollution is worsening air quality from higher concentrations of ground level ozone and inhalable fine and ultrafine particles.[58, 59] This ‘dirty air’ is reported to disproportionately impact the health of the most vulnerable sector of society including kids, elderly, the poor, and people of color around the world.[58, 59] According to the World Health Organization [60] and the Lancet report on pollution and health by the Global Alliance on Health and Pollution,[61] outdoor and indoor air pollution is the cause of over one-third of deaths from stroke, lung cancer, and chronic respiratory disease, and one quarter of the deaths from ischaemic heart disease. Inhaling fine particulate matter has been linked to cardiovascular, respiratory, nervous and reproductive diseases leading to cancers and premature deaths.[25] In 2016, 600,000 children died from acute lower respiratory infections caused by polluted air. Respiratory viruses including the SARS-Cov-2 and influenza viruses are spread through airborne transmission of virus-laden aerosols and air pollution PM.[62] In light of the ongoing global COVID-19 pandemic, a study has detected the SARS-Cov-2 virus on air pollution PM, which could have enabled the spread of the virus causing higher rates of infection.[63] The reference PM instruments provide data on the mass concentration of PM_{10} and $PM_{2.5}$ and not their chemical or biological composition, which is directly linked to their chemical toxicity and health impacts upon inhalation.[64-66] Given the complexity in the chemical composition of PM, Park *et al.*[67] analyzed the differential toxicity of fine particulate matter from various combustion and non-combustion sources to derive toxicity scores. They reported that the highest toxicity scores are obtained from traffic related $PM_{2.5}$.

Examples of the chemical species of special interest to air quality research are shown in Fig. 3. Transition metals in PM include redox active Fe, Cu, Mn, and Ti with varying amounts. The transition metal content in urban PM originates mainly from soil, road dust, break and tire wear[68] and has high levels of transition metals such Fe and Cu.[69] These metals can generate reactive oxygen species such as hydroxyl radicals and hydrogen peroxides that are the main culprits for PM chemical toxicity upon inhalation.[64, 70-73] These species are important players in the redox chemistry in wet aerosols that affect the solubilization of Fe during transport, which affect the biogeochemical effect of aerosol deposition (see section 3.3). Transition metals can be 'soluble' in simulated lung or biological fluids[74] which leads to toxicity. Chemical toxicity studies assess bioaccessibility of metals in PM use assays to quantify the fraction of soluble metal to accurately estimate the oxidative potential following inhalation-ingestion.[6, 75] Most of the anions and organic acids in PM (described in detail below) are strong chelating agents for transition metals, and hence, identifying and quantifying their concentrations affect the bioavailability of metals and redox potential of PM.[76] Tacu *et al.*[6] focused their toxicity studies on oxidative potential of Fe and Cu in the soluble fraction and surface of carbonaceous ultrafine particles. They found that surface Fe(II) induces inflammation and DNA damage, whereas Cu(I) is more reactive

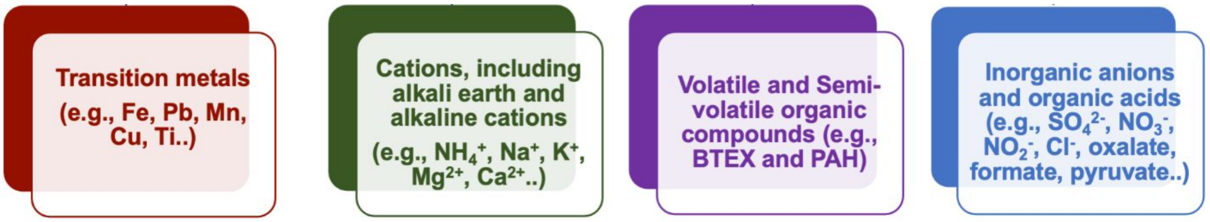

Fig. 3: Illustration highlighting the chemical composition of PM important for understanding their health impacts. BTEX = benzene, toluene, ethylbenzene and xylene

in oxidative stress and cytotoxicity. Their findings lead to the conclusion that total metal in PM is a better indicator of pathogenicity than water-soluble metals. This experimental approach that seeks to disentangle the role of soluble versus the particle fraction of metals is similar to what is done in the ocean biogeochemistry community, where different leaching methods are used to extract ‘trace metals’ from filters containing dust particles to assess their bioavailability to organisms in the sea surface microlayer.[31, 77]

Also shown in Fig. 3 are sulfate, nitrate, and nitrite form in atmospheric PM from secondary condensed phase oxidation of sulfur and nitrogen oxides.[33] Non-sea salt components such as chloride, Na^+, Mg^{2+}, Ca^{2+} in urban PM originate mainly from run off and road salt.[78] The ammonium content in PM originates from the partitioning of gas phase ammonia emitted mainly from agricultural and animal husbandry sources.[79] Organic anions are mainly the conjugated bases of carboxylic acids that form in PM from secondary condensed phase oxidation of the organic content of PM from primary (e.g., traffic) and secondary sources.[80] Volatile and semi-volatile organics such as isoprene, glyoxal, catechol, and benzene, toluene, ethylbenzene and xylene **(**BTEX) are reactive gases are emitted from biogenic and anthropogenic sources. Polyaromatic hydrocarbons (PAHs) have also been detecting in urban PM.[81] This section highlights that at a molecular level, chemical reactions of interest to toxicologists and health experts are the same as the ones of interest to atmospheric chemists and ocean scientists. The following sections describe in detail the climate and ocean impacts of Fe-containing aerosol particles highlighting the importance of Fe chemistry.

3.2 Climate impacts

The climate impacts of Fe-containing aerosol particles and droplets reinforce the interplay between aerosol-radiation interactions (direct effect), aerosol-cloud interactions (indirect effect), and oceanic uptake of CO_2. The direct effect refers to aerosols' role in interacting with solar and terrestrial radiations, which is influenced by their optical properties. Mineral dust particles weakly absorb visible radiation, and hence their single scattering albedo, which depends on particle size and mineralogy (specifically the hematite and goethite content)[82], is typically in excess of 0.95 at the peak of the solar spectrum.[28, 29] However, dust models typically underestimate the coarse dust load, which absorbs shortwave radiation more efficiently than finer particles.[83] Current models need to improve their ability to capture the evolution of the coarse dust in order to quantify the role of Fe oxides in determining the shortwave absorption.[84]

Field measurements coupled with electron microscopy images of particle chemical composition and morphology showed that trace gases, volatile organic compounds , and soot are efficiently take up and mixed with dust particles in Asian outflows. [46, 85] This evolution of dust particles is manifested by complex morphologies with light-absorbing inclusions that have strong effect on dust optical properties that decreases single scattering albedo for smaller particle size [26]. As detailed elsewhere[48, 55], the Fe content in aged mineral dust could catalyze (photo)chemical reactions with organics though multiphase chemistry that also changes dust optical properties.

The indirect effect of Fe-containing aerosol particles on the climate refers to their hygroscopic properties that influence ice and cloud condensation efficiencies and modify cloud formation and lifetime.[86] Although 'fresh' mineral dust particles have poor hygroscopicity, they are considered efficient ice nuclei.[86] Chen *et al.*[87] reported the hygroscopicity of seven mineral dust samples from Africa, Asia and North America following characterization of their Brunauer-Emmett-Teller (BET) surface area, average particle diameter, and mineralogy. They found a wide range of mass ratios of adsorbed water to the dry mineral at 90% relative humidity from 0.0011 to 0.3080 due to differences in the BET surface areas indicating poor hygroscopicity.[87] Comparison of results from other research groups revealed some degree of discrepancy in the hygroscopicity parameterizations. This discrepancy was attributed to differences in samples and pre-treatment procedures used by each group. This example highlight future work would benefit from distributing same samples among different groups and standardizing sample pre-treatment methods and for the water uptake data to be normalized to surface area of the material.[86, 87]

As Fe-containing aerosol particles age in the atmosphere due to multiphase chemistry and particle mixing, they become more hygroscopic and their ice nucleation efficiencies change due to the increased concentration of salts and oxidized organics (see reviews [48, 86]). To mimic heterogeneous multiphase chemistry in freshly-emitted and aged dust particles, the lab experiments summarized in reference[48] used hematite, Arizona test dust (5% Fe by weight), and $FeCl_3$ as sources of insoluble and soluble Fe(III). Organics used to study Fe-driven reactions included surface active phenolic compounds identified in biomass burning organic aerosol extracts, precursors for secondary organic aerosols, and aliphatic dicarboxylic acids from the transformation of volatile organic compounds and aging of secondary organic aerosols. These reactions were shown to result in oligomerization and polymerization of organic precursors forming colored soluble and insoluble products. These products were found to be slightly hygroscopic under sub- and supersaturated relative humidity with hygroscopicity parameter ranges from 0.03 to 0.25, which is within that for secondary organic aerosols.[88] The ice nucleation efficiency of Arizona test dust was not significantly affected by the polymerization products compared to unreacted dust.[89] The polymerization products have mass absorption coefficients between 290 and 400 nm, which is on the same order of magnitude as brown carbon from primary sources, highlighting the interplay the direct and indirect effects of Fe-containing aerosol on the climate due to the role of Fe in aging processes as a catalyst (see review [48]).

Studies have shown that the atmospheric deposition of mineral dust from natural and anthropogenic sources to the oceans can affect the direct forcing of climate through its impact on ocean productivity and atmospheric CO_2 uptake, and influence the climate feedbacks through its effect on ocean ecosystem diversity.[31] The following section describe in detail the impact of Fe-containing aerosol on the ocean.

3.3 Ocean impacts

All known forms of life require Fe to carry out several physiological functions. Acquisition of Fe by aquatic microorganisms is particularly difficult, as the oxidizing environment of the oceans limits concentrations of aqueous inorganic Fe to sub-nanomolar levels, orders of magnitude less than what is required to sustain oceanic biomass and primary production.[90, 91] Because of this, different phytoplankton species developed varying mechanisms for in situ biological Fe uptake. Some excrete complex organic molecules, siderophores, that can help to mobilize Fe from particulate forms in seawater and keep it in dissolved form[92], while others developed adaptive strategies that enhance iron dissolution from oxides and dust through cell-surface processes.[93]

Therefore, characterization of the ocean's biogeochemical cycle of Fe requires quantitative knowledge of atmospheric sources and chemical speciation of Fe as well as surface ocean photochemistry, aquatic geochemistry, molecular biology, and chemical and biological oceanography. Achievements of the past decade of laboratory studies, field measurements, and modeling research with a particular emphasis on global biogeochemical cycling of Fe in the oceans were summarized in a report from an international workshop that was convened in Telluride, Colorado on July 30–August 3, 2018.[31] To gain a better understanding of the possible roles and sensitivities of aerosol Fe input into the different regions of the ocean, it was suggested that future field/laboratory studies and model simulations should strive to better represent (1) the bioavailability of colloidal/nanoparticulate and dissolved Fe for different phytoplankton species, (2) Fe-chelating organic ligands in the surface microlayer and the bulk of the ocean, and (3) the timescales and variable/reversible scavenging rates of dissolved Fe from seawater.[31] The workshop participants agreed that existing challenges and disconnects (both fundamental and methodological) are undoubtedly caused by extremely low concentrations, short lifetime, and the myriad of physical, (photo)chemical, and biological processes affecting the global biogeochemical cycling of Fe. However, it was also pointed out that the historical division (separate treatment of Fe biogeochemistry in oceanic and atmospheric disciplines) and the classical funding structures (that often create obstacles for transdisciplinary collaboration) are hampering the advancement of knowledge in the field.

Significant improvements have been achieved in the representation of Fe biogeochemistry over the past couple of years. Models now incorporate the role of combustion Fe-containing aerosol particles in the oceans[94], though a research gap remains in understanding the characteristics of nutrients released from fires and industrial or vehicular sources. The reproducible methods have been developed to characterize some of the classes of organic compounds complexing Fe in seawater and aerosols. However, as most of the operationally- (electrochemically-) defined Fe binding ligands in seawater remain uncharacterized, laboratory and field incubations and process studies are recommended to target certain ligands and oceanic regimes. There is also a need to better quantify organic ligands through intercomparison of the various measurement techniques in the ocean, aerosols, and rain. More research is also needed on the longer-term fate of Fe-containing aerosol particles during its weeks to months residence time in the ocean surface mixed layer. This includes the effects of marine particles and the sea-surface microlayer on Fe-containing aerosol particles biogeochemistry. In the sunlit water column particularly, the roles played by microorganisms in altering Fe-containing aerosol particles bioavailability and residence time, particle micro-environments, aggregation/disaggregation, size (including colloids), the chemical composition and thickness of the surface microlayer, and the effect of microplastics should be investigated. Several fundamental questions related to ocean fertilization by mineral dust also remain unresolved. For example, if Fe-complexing ligands are produced by phytoplankton in response to dust deposition events, how much of this Fe-containing aerosol particles can be transferred to the dissolved phase, and is this solubilized dissolved Fe is then bioaccessible to the entire microbial community remains an open question. It is now well recognized that in addition to Fe, atmospheric deposition of natural and anthropogenic aerosols brings biologically essential (and potentially toxic) trace elements (e.g., Mn, Co, Ni, Cu, Zn, Cd, Pb) to the oceans where they influence the growth of phytoplankton and bacteria. Future experimental approaches and model simulations need to also consider the possible toxicity and biological competition/co-limitation effects of these trace elements, ligands, and organic compounds. Pushing the boundaries of transdisciplinary research helps scientists to shed the light on important insights into how aerosol Fe deposition from the atmosphere may impact the ocean microbial community and the global carbon cycle.

4. Complexity of the mineral-organic-water interface in atmospheric aerosols

Processing of Fe-containing aerosol particles takes place in the atmosphere through heterogeneous reactions with acidic gases, organics, in the dark or under irradiation, changing the chemical composition of the gas phase and the hygroscopicity of these particles that increases the amount of dissolved Fe in aerosol liquid water.[95-99] Mechanistic level understanding of these gas/adsorbed water/(semi-)solid reactions of atmospheric relevance benefits from decades of work by geochemists and soil scientist who study the liquid/mineral interface using surface sensitive spectroscopic and molecular modeling techniques.[13, 100, 101] For example, Fig. 4 represents critical factors in Fe solubility and bioavailability in the surface oceans that seem to be under-studied in field and experimental work. The two issues are these: size characterization generally misses ultrafine particles attached to larger particles, and soil processes are likely to lead to surface chemistries different from the bulk that may be kinetically recalcitrant. Without detailed characterization of the surface chemical composition in studies that examine Fe solubility and biological effects, one cannot truly characterize the mechanisms of Fe removal from the aerosols. Studying aerosol particle surfaces with nanoscale secondary ion mass spectrometry (nanoSIMS) (for example, see ref. [11, 12, 102]) and other ambient pressure surface techniques in collaboration with field researchers, climate modelers and health scientists will be required to produce completer and more detailed picture of mineral aerosol effects and impacts.

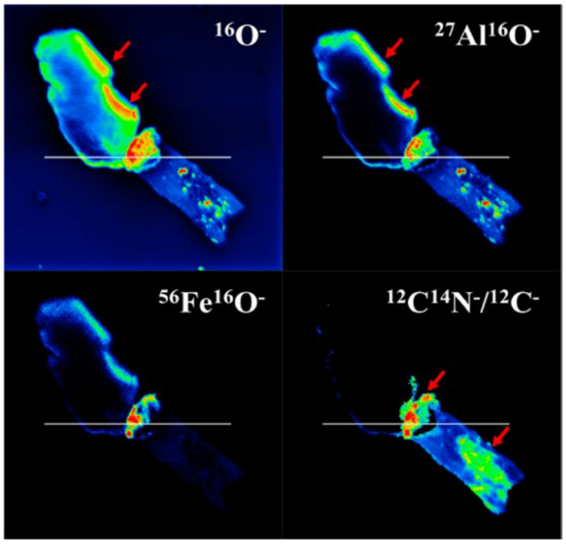

Fig. 4. NanoSIMS measurements of the soil cluster shown in panels b–d of Figure 3 in ref. [11]. The three fragments are identified as one clean mineral affected in the center by charging, an organo-mineral association, and a thick organic matter patch with mineral crumbs without charging effects. Reprinted (adapted) with permission from Höschen, C.; Höschen, T.; Mueller, C. W.; Lugmeier, J.; Elgeti, S.; Rennert, T.; Kögel-Knabner, I., Novel sample preparation technique to improve spectromicroscopic analyses of micrometer-sized particles. *Environ. Sci. Technol.* **2015,** *49* (16), 9874-9880. ©2015 American Chemical Society.

In addition to the complexity of mineral aerosol surface chemistry, the organic biogeochemistry associated with soil processes and surface oceans includes a vast array of potential ligands. Mineral coatings are comprised of a range of molecular weight compounds. Experimental studies that characterize ligand (e.g., oxalate) and siderophore effects should consider the differences between ‘aged’ natural samples whose surface chemical composition differs from the bulk and fresh lab-synthesized particles. Oxalate is a common and strong Fe-binding ligand under acidic conditions, but fulvic and humic acids have aromatic ligands similar to salicylic acid that strongly chelate Fe over a wide pH range. Fourier-transform ion cyclotron resonance mass spectrometry can be used to identify key functional groups in natural systems for inclusion in more controlled experiments, computational chemistry studies on equilibrium and rate constants, transport modeling, and mathematical thermodynamic and kinetic speciation modeling.

While a reductionist approach at the ligand level would provide invaluable insights on Fe fate in aerosol and ocean environments, examining the effect of microbes and plankton on these molecular level processes is also needed. With the increase in the application of machine learning to environmental research, new data should come from experiments, and modeling using multicomponent systems under realistic conditions and times relevant to those in the field.

Recommendations for future research

Scientists are receptive to the idea of a larger community network that strives to organize studies, data collection and sharing, and field, experiment, and modeling work. Fig. 5 illustrates the major processes that need study in an integrated manner and in a way that the puzzle pieces referred to in the recent Intergovernmental Panel on Climate Change report[103] can be put together at the end of the day. There is the potential for this, but unless funding agencies support long-term, transdisciplinary, and international research, we may pass the climate "tipping points".[104] There are many applications (e.g., modeling radiative effects, cloud condensation effects, health effects, ocean productivity, geoengineering, etc.) that could use the same data, so justifications for allocating funds for an inter- and multi-disciplinary community collaborative effort are strong and warrant advocating for connected research plans to transfer data and information from one team to another.

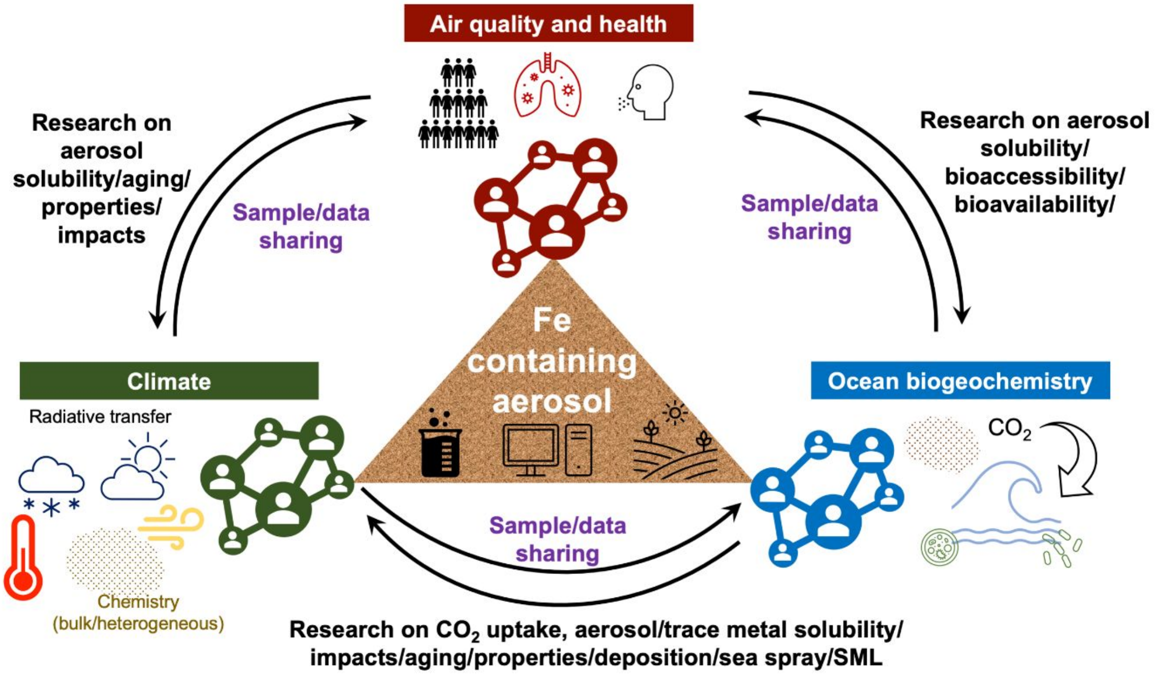

Fig. 5. Schematic highlighting the interconnectedness of scientific fields with experts engaged in understanding the impacts of Fe-containing aerosol. 'Research' refers to lab studies using model systems, field campaigns that collect samples from different sources and impacted locations, computational chemistry and modeling from the molecular to the regional and global scales of atmospheric chemistry/ocean/climate systems. Modeling also includes statistical calculations and predictions of population exposure and health outcomes. We are calling for the creation of a network that connects experts engaged in the source to sink Fe-containing aerosol to facilitate knowledge exchange through sample and data sharing.

Laboratory investigations to date on model systems show that Fe oxides may not be the only source of insoluble iron in aerosols that enter the ocean. Fe-containing organic polymers could be there from secondary processes. [48] We recommend that future laboratory studies on Fe sources to the ocean from atmospheric deposition of 'aged' aerosols be conducted with standard samples across different labs (dust, organic compounds, and biological materials), and measure the kinetics and thermodynamics of *'aged' dust dissolution* as a function of pH, ionic strength, and light. Ligand exchange efficiency of *soluble Fe complexes* need to be measured over short- and long-time frames as a function of pH, ionic strength, light, and organic matter structure in single and multicomponent systems. These lab studies need to be complemented by molecular and mathematical modeling to fully understand the underlying driving forces for lab observations and create accurate predictive models at each scale. In addition, we recommend that atmospheric chemistry models include relative humidity and size-dependent aerosol water content in Fe-containing particles because it affects acidity, ionic strength, type of chemical reactions. These atmospheric chemistry models also need to include mechanisms for Fe-driven particle growth and aging, and stability constants for Fe complexes with organic ligands detected in field aerosols.

Moreover, we recommend that future research should also focus on biogeochemical cycling of Fe at the air-sea interface focus (on the time scale of minutes to days and at the spatial resolution of tens of meters to kilometer), in the zone that is often overlooked in global atmospheric an oceanic models.[105] Such research should focus on the interaction of wet and dry-deposited ‘aged dust’ with the sea surface microlayer functional groups representative of organics and biota in the sea surface microlayer , organic ligand-promoted, and photo-reductive mechanisms, availability of strong and weak organic ligands in the surface ocean, and bioaccessibility(availability) of transition metals over short- and long-time scales

Author contributions

All authors conceived the ideas presented in this paper, and contributed to the writing and editing.

Conflicts of interest

There are no conflicts to declare.

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