**SPECIATION OF Fe IN
AMBIENT AEROSOL AND CLOUDWATER**

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ABSTRACT

Atmospheric iron (Fe) is thought to play an important role in cloudwater chemistry (e.g., S(IV) oxidation, oxidant production, etc.), and is also an important source of Fe to certain regions of the world's oceans where Fe is believed to be a rate-limiting nutrient for primary productivity. This thesis focuses on understanding the chemistry, speciation and abundance of Fe in cloudwater and aerosol in the troposphere, through observations of Fe speciation in the cloudwater and aerosol samples collected over the continental United States and the Arabian Sea. Different chemical species of atmospheric Fe were measured in aerosol and cloudwater samples to help assess the role of Fe in cloudwater chemistry. Chapter 2 presents a set of experiments which used ambient aerosol samples suspended in aqueous solution and then irradiated with uv-light to simulate cloudwater conditions. These experiments found Fe to be a critical component for the production of H_2O_2 . Chapter 3 discusses the development and application of a novel photochemical extraction method for the determination of photochemically-available Fe in ambient aerosol samples. Photochemically-available Fe ranged from $< 4 \text{ ng m}^{-3}$ to 308 ng m^{-3} , and accounted for 2.8% to 100% of the total Fe in aerosol samples collected in California and New York. Calculations based on the results of these experiments predicted that redox reactions of Fe in cloudwater could be an important in situ source of oxidants ($\cdot\text{OH}$, $\text{HO}_2\cdot/\text{O}_2\cdot^-$). Chapter 4 presents results of several field studies which measured the redox states of Fe and other transition metals (Mn, Cu and Cr) in cloudwater. These measurements were then used in thermodynamic models which predicted Fe(III) to be either as Fe(III)-hydroxy species or Fe(III)-oxalate species. However, an un-identified strong chelating ligand with Fe(III) was also suggested by the thermodynamic model results. Chapter 5 presents results of a field study conducted on the Arabian Sea. Total atmospheric labile-Fe(II) ranged between $< 0.09 \text{ ng m}^{-3}$ to 7.5 ng m^{-3} during the inter-monsoon period, and was consistently below the

detection limit during the southwest-monsoon period. The labile-Fe(II) measured during the inter-monsoon period was predominantly found in the fine fraction of the aerosol. Principal component analysis revealed a significant source of Fe and Mn which was not associated with the main aeolian dust component.

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Chapter 1:

Introduction and Overview

PREFACE

This thesis, "Chemical Characterization of Iron in Atmospheric Cloudwater and Aerosols," consists of four papers. I was first author on all four of these papers. The first paper (Chapter 2) was published in *Geochimica et Cosmochimica Acta*, the second paper (Chapter 3) was published in *The Journal of Geophysical Research*, the third paper (Chapter 4) is ready for submission to *The Journal of Air and Waste Management*, and the fourth paper (Chapter 5) is ready for submission to *The Journal of Geophysical Research*. Much of this thesis centers around the analysis of aerosol and cloudwater samples collected over the continental United States and the Arabian Sea. I was involved in every component of this research. These components included: 1) aerosol collector design and construction, 2) field preparation, 3) coordination of field studies with other scientists, ship masters, etc., 4) sample collection, 5) sample analysis, 6) thermodynamic and kinetic modeling, 7) statistical analysis, and 8) manuscript writing. Due to the location and duration of the numerous field studies included in this thesis, other people also helped significantly in the collection and chemical analysis of samples. These people included: Anne M. Johansen, Simo O. Pehkonen and Samuel M. Webb. While working on this thesis I also contributed to several other papers and projects related to this thesis, but not included. I was second-author on two papers which involved laboratory studies which were relevant to the atmospheric chemistry of Fe. These papers were titled: "Photoreduction of iron oxyhydroxides and photooxidation of halogenated acetic acids: Implications for tropospheric chemistry" [Pehkonen et al., 1995], and "Photoreduction of iron oxyhydroxides in the presence of important atmospheric organic compounds" [Pehkonen et al., 1993]. Both of these papers were published in *Environmental Science and Technology*.

INTRODUCTION

Cloudwater and aerosol chemistry is a poorly understood component of atmospheric chemistry compared to gas-phase atmospheric chemistry. Recent discoveries of sulfur oxidation in clouds ("acid rain") and the role of polar stratospheric clouds (PSCs) in stratospheric ozone chemistry have revealed the importance of cloudwater and aerosol chemistry in the troposphere and stratosphere. Atmospheric Fe is thought to play an important role in cloudwater chemistry (including sulfur oxidation, organic acid production and destruction, and oxidant production and destruction), and is also an important source of Fe to certain regions of the world's oceans where Fe is a rate-limiting nutrient for primary productivity. This thesis focuses on the understanding the chemistry and abundance of Fe in cloudwater and aerosol in the troposphere, through observations of Fe speciation in the cloudwater and aerosol samples collected over the continental United States and the Arabian Sea.

Background

In order to understand the chemistry occurring in clouds and aerosols, the detailed chemical speciation of transition metals (e.g., Fe, Mn, Cu, and Cr) must be understood. A knowledge of the transition metal chemical species (for all oxidation states) as a function of variables such as pH, organic ligands, and inorganic ligands is critical to the assessment of atmospheric reaction pathways involving S(IV), O₂, R₂CO, NO_x, ROOH and H₂O₂ in heterogeneous phases. In addition, a knowledge of the detailed chemical speciation of Fe is also important to the assessment of the ability of marine biota to utilize atmospherically-derived trace elements as micronutrients.

Iron (Fe) is the fourth most abundant element in the earth's crust and the most abundant first-row transition element. Because of its abundance in the earth's crust, Fe is

also the most abundant first-row transition element in atmospheric aerosols since, on a global scale, aeolian dust is a major source of refractory elements to the atmosphere. The next three abundant first-row transition elements in the atmosphere are Mn, Cu and Cr. Several studies have investigated the particle size distribution and source identification of these transition metals in the atmosphere [Galloway *et al.*, 1982; Lantzy and Mackenzie, 1979; Nriagu, 1989; Nriagu and Davidson, 1986; Puxbaum, 1991]. But only a few studies have looked at the speciation or reactivity of trace metals in the fogwater or cloudwater [Behra and Sigg, 1990; Erel *et al.*, 1993; Kotronarou and Sigg, 1993; Xue *et al.*, 1991] or in ambient aerosol [Kopcewicz and Kopcewicz, 1991; Kopcewicz and Kopcewicz, 1992; Siefert *et al.*, 1994; Spokes *et al.*, 1994; Zhu *et al.*, 1993; Zhuang *et al.*, 1992].

Iron is predominantly found as either ferric iron (Fe(III)), or ferrous iron (Fe(II)) in the earth's crust, lakes and oceans. Mn, Cu and Cr can also be found in several oxidation states in natural waters: 1) Mn as Mn(II), Mn(III) and Mn(IV), 2) Cu as Cu(I) and Cu(II), and 3) Cr as Cr(III) and Cr(VI). These metals are known to participate in a variety of redox reactions in natural waters involving S(IV), organic compounds, oxidants and metal ions [Conklin and Hoffmann, 1988; Faust and Hoffmann, 1986; Graedel *et al.*, 1986; Weschler *et al.*, 1986; Wiersma and Davidson, 1986]. Fe and Mn are also found as particulate oxides and hydrous oxides in natural waters, which can also participate in a variety of redox reactions on the surface of these particles which are similar to those of dissolved Fe and Mn [Faust and Hoffmann, 1986; Kieber and Helz, 1992; Regazzoni and Blesa, 1991; Siefert and Sulzberger, 1991; Stone, 1986].

Figure 1 shows an overview of Fe in the atmosphere. Sources of Fe and other transition elements to the atmosphere include: aeolian dust, volcanic activity and anthropogenic sources [Nriagu, 1989; Nriagu and Davidson, 1986; Puxbaum, 1991]. Meteoritic Fe is also a detectable source of Fe to the atmosphere [Kopcewicz and Kopcewicz, 1992]. Once in the atmosphere Fe can be cycled between "dry" aerosol

particles (hereafter referred to as aerosol particles) and cloudwater droplets. "Dry" refers to atmospheric conditions where the relative humidity is not high enough (i.e., supersaturation conditions) for the aerosol particles to grow to cloud-size drops. These "dry" aerosol particles can be incorporated into cloud droplets by either the aerosol particle serving as a nucleus for a cloud drop, or an interstitial aerosol particle impacting on pre-existing cloud drop. Overall, aerosol particles undergo an estimated of 10 nucleation/evaporation cycles before they are removed from the atmosphere by wet or dry deposition [Junge, 1964]. Once in a cloud droplet, Fe can be involved in S(IV) oxidation, organic acid production/destruction, and oxidant (e.g., $\cdot\text{OH}$, HO_2) production/destruction [Graedel *et al.*, 1986; Faust, 1994; Jacob *et al.*, 1989]. This chemistry can also potentially change the speciation or mineral form of Fe present in the atmosphere, effectively "weathering" the Fe as it is advected. Finally, the Fe is removed from the atmosphere through either wet or dry deposition. This deposition is critical to certain regions of the oceans where Fe is a rate-limiting nutrient to phytoplankton growth and therefore determines the primary productivity of these regions of the oceans [Ditullio *et al.*, 1993; Kolber *et al.*, 1994; Martin *et al.*, 1994; Martin and Gordon, 1988; Price *et al.*, 1994]. The metal speciation is critical to the ability of the marine biota to utilize atmospherically-derived trace elements as micronutrients [Hudson and Morel, 1990; Hudson and Morel, 1993; Morel *et al.*, 1991; Wells *et al.*, 1994; Wells *et al.*, 1995]. The primary source of Fe to these regions of the oceans is through atmospheric deposition.

Thesis Work

The goal of this thesis was to characterize atmospheric Fe, along with various other species relevant to the chemistry of Fe, in cloudwater and aerosol to help understand the role of Fe in heterogeneous atmospheric chemistry, and also its role as a nutrient source to surface ocean waters. This goal was achieved by the development and application of several collection and analytical methods. These methods were used in a multitude of field

studies to investigate Fe speciation in aerosol and cloudwater. Figure 2 outlines the different measurements conducted for Fe in ambient aerosol samples. Figure 3 outlines the different measurements conducted for Fe in cloudwater samples.

The second chapter discusses experiments using atmospheric aerosol samples collected from Whiteface Mtn. (NY), Pasadena (CA), and Sequoia National Park (CA). The aerosol samples were suspended in aqueous solutions ("simulated cloudwater"), followed by addition of various organic acids (oxalic, formic and acetic acids), which are commonly observed in cloudwater. The solution was then irradiated with ultraviolet light (similar intensity to ambient sunlight) and various species were measured (i.e., H_2O_2 , $\text{Fe(II)}_{\text{aq}}$ and pH). These experiments found Fe to be a critical component for the production of H_2O_2 in the simulated cloudwater experiments.

The third chapter discusses the development and application of a novel photochemical extraction method for the determination of photochemically-available Fe. This method was used to characterize Fe in aerosol samples collected from Whiteface Mtn. (NY), Pasadena (CA), San Nicholas Island (CA) and Yosemite National Park (CA). Several aerosol samples were collected during biomass burning episodes. Photochemically-available Fe ranged from $< 4 \text{ ng m}^{-3}$ to 308 ng m^{-3} , and accounted for 2.8% to 100% of the total Fe in the sample. Calculations based on the results of these experiments predicts that redox reactions of Fe in cloudwater could be an important in situ source of oxidants ($\cdot\text{OH}$, $\text{HO}_2\cdot/\text{O}_2\cdot$).

The fourth chapter discusses results of several field studies which measured the redox states of Fe and other transition metals (Mn, Cu and Cr) in cloudwater. Other measurements, relevant to the speciation and redox chemistry of these metals, included: pH, total elemental concentrations, organic anions, inorganic anions, cations, peroxides, and formaldehyde. Several cloud events were sampled at Whiteface Mtn (NY), San Pedro Hill (CA) and Bakersfield (CA). The results of the measurements were then used in thermodynamic models to calculate the speciation of the metals in the cloudwater samples.

Fe(III) was found to occur either as Fe(III)-hydroxy species or Fe(III)-oxalate species. However, an un-identified strong chelating ligand with Fe(III) was also suggested by the data. A kinetic model was also used to investigate the metal redox chemistry.

The fifth chapter discusses results of a field study conducted aboard the research vessel Meteor on the Arabian Sea. Aerosol samples were collected and immediately analyzed for labile-Fe(II) fractions (along with other important species) during two separate cruises in 1995. The first cruise occurred during the inter-monsoon period and the second occurred during the southwest-monsoon. A high volume dichotomous virtual impactor (HVDVI) was used to collect aerosol in the fine and coarse fractions. Total atmospheric labile-Fe(II) ranged between $< 0.09 \text{ ng m}^{-3}$ and 7.5 ng m^{-3} during the inter-monsoon period, and was consistently below the detection limit during the southwest-monsoon period. The labile-Fe(II) measured during the inter-monsoon period was found predominantly in the fine fraction of the aerosol. Principal component analysis revealed a significant source of Fe and Mn which was not associated with the main aeolian dust component.

Overall, this thesis has provided further insight into cloudwater and aerosol chemistry in the atmosphere. However, more sensitive analytical methods, better collection techniques, and laboratory experiments will certainly bring new discoveries regarding these complicated dynamic systems.

FIGURE CAPTIONS

FIGURE 1 Overview of atmospheric iron.

FIGURE 2 The different measurements conducted for Fe in ambient aerosol samples.

FIGURE 3 The different measurements conducted for Fe in cloudwater samples.

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Figure 1

Figure 2

Fe ANALYSIS IN AEROSOL SAMPLES

Figure 3

Fe ANALYSIS IN CLOUDWATER SAMPLES

Chapter 6:

Conclusions and Future Work

CONCLUSIONS

Experiments, using ambient aerosol samples suspended in aqueous solutions to simulate cloudwater chemistry, along with the measurement of different chemical species of Fe in aerosol and cloudwater samples, were used to assess the role of Fe in cloudwater chemistry. These measurements included several labile fractions of Fe(II) and photochemically-available Fe. Many other species, relevant to the chemistry of Fe, were also measured. The aerosol and cloudwater samples were collected from a variety of locations to understand spatial variability. The sampling sites included: Pasadena (CA), San Nicholas Island (CA), Sequoia National Park (CA), Yosemite National Park (CA), Whiteface Mountain (NY), and the Arabian Sea. Thermodynamic and kinetic models, along with statistical methods were used to interpret the field observations.

Experiments to simulate cloudwater conditions were carried out by suspending ambient aerosol samples in an aqueous solution and then irradiating the solution with ultraviolet light. A total of four different ambient aerosol samples were used in the simulated cloudwater experiments; they were collected from Whiteface Mountain, NY (1), Pasadena, CA (2) and Sequoia National Park, CA (1). In all cases, the production rates for Fe(II)_{aq} and H₂O₂ in the light were greater than production rates in non-irradiated control experiments. The simulated cloudwater experiments (with 4 different aerosol samples) showed similar behavior to previous experiments carried out with synthetic Fe-oxyhydroxy polymorphs in the presence of oxalate, formate or acetate. The Fe present in the ambient aerosol appears to be a critical component for the production of H₂O₂ in the simulated cloudwater experiments.

A novel photochemical extraction procedure was developed and used to determine the concentration of photochemically-available Fe in ambient aerosol samples. Ambient aerosol samples, collected at Whiteface Mountain (NY), Pasadena (CA) and San Nicholas

Island (CA), were suspended in an aqueous solution within a photochemical reactor and irradiated. Under these conditions, which were favorable to the photo-chemical weathering of aerosol particles, the relative amount of $\text{Fe(II)}_{\text{aq}}$ to Fe_{total} was shown to increase and used to characterize the Fe in the aerosol samples. Photochemically-available Fe concentrations found ranged from $< 4 \text{ ng/m}^3$ to 308 ng/m^3 and the percentage of photochemically-available Fe to Fe_{total} ranged from 2.8% to 100%. Aerosol samples were also collected during biomass burning events in Southern California; these samples showed insignificant changes in the photochemically-available Fe (compared to non-biomass burning samples) in conjunction with large increases of Fe_{total} . Calculations based on these experiments also provides further evidence that redox reactions of Fe in cloudwater could be an important *in situ* source of oxidants ($\cdot\text{OH}$, $\text{HO}_2\cdot/\text{O}_2\cdot$).

Other transition metals also may play an important role in the atmospheric chemistry of Fe. Therefore, the oxidation state of Fe and three other transition metals (Mn, Cu & Cr) in cloudwater were investigated during several cloud events at Whiteface Mountain (NY), one cloud event at San Pedro Hill (CA) and one fog event at Bakersfield (CA). Other measurements performed, relevant to the redox chemistry of these metals, included pH, total elemental concentrations (Fe, Cu, Mn, Cr, Al, K, Ca, Na and Mg), organic anions (formate, acetate, glycolate, oxalate), inorganic anions (chloride, sulfate, nitrate, sulfite), cations (sodium, calcium, magnesium, potassium), peroxides, and formaldehyde. These measurements were then used in thermodynamic speciation models to understand the speciation of ambient fog and cloudwater. From this analysis, two different cases were found for $\text{Fe(III)}_{\text{soluble}}$ speciation. Fe(III) was found to exist either as Fe(OH)_2^+ or Fe(Oxalate)_2^- . However, an un-identified strong chelating ligand with Fe(III) was also suggested by the data. Cu(I) and Cu(II) were calculated to be predominantly Cu^+ and Cu^{2+} (with less than 10% as Cu(II)-oxalate complexes). A chemical kinetic model was also used to investigate the transition metal chemistry. The model results indicate Fe(II) should be the predominant chemical form of Fe during daylight conditions. This prediction is in

agreement with the field measurements in which the highest ratios of $\text{Fe(II)}/\text{Fe}_{\text{total}}$ were found in samples collected during the day. The model results also indicated Fe(III) should be the predominant form of Fe during nighttime conditions, this is also in agreement with the field measurements. In the model, Cu(II) and Mn(II) were the predominant oxidation states during daylight and nighttime conditions, with Cu(I) and Mn(III) increasing during daylight conditions. Mn(III) concentrations were never high enough to influence the redox chemistry of Cr. Overall, Cr(VI) in cloudwater is predicted to be reduced to Cr(III) .

Ambient aerosol samples were also collected during the inter-monsoon and southwest-monsoon periods on the Arabian Sea. A high-volume dichotomous virtual impactor (HVDVI) with an aerodynamic cutoff size of $3\ \mu\text{m}$ was used to collect the fine and coarse aerosol fractions for metal analysis. A low volume collector (LVC) was used to collect aerosol samples for anion and cation analysis. The primary purpose of this study was to characterize the chemical composition of the ambient aerosol during the southwest-monsoon and inter-monsoon periods, including the measurement of labile ferrous iron (Fe(II)) in the fine and coarse fractions of ambient aerosol samples. The analysis for labile- Fe(II) was done immediately after sample collection to minimize any possible Fe redox reactions which might occur during sample storage. Total atmospheric aqueous labile- Fe(II) concentrations during the inter-monsoon period were between $7.48\ \text{ng m}^{-3}$ to $< 0.089\ \text{ng m}^{-3}$. The aqueous-labile Fe(II) was predominantly in the "fine" fraction ($< 3.0\ \mu\text{m}$), with the "fine" fraction of aqueous labile Fe(II) accounting for an average of 90% of the total aqueous labile Fe(II) . In contrast, during the southwest-monsoon period, the atmospheric aqueous labile Fe(II) concentrations were consistently below the detection limit ($< 0.34\ \text{ng m}^{-3}$ to $< 0.089\ \text{ng m}^{-3}$ depending on the volume of air sampled). Factor analysis revealed a significant source of Fe and Mn which was not associated with the main aeolian dust component or any typical anthropogenic metals (e.g. V, Pb). This component did not include any loadings of labile- Fe(II) . The air mass back trajectories (5 day, three-dimensional) showed that air masses sampled during the southwest-monsoon had origins

over the open Indian Ocean, and air masses sampled during the inter-monsoon had origins from southeast Africa, Saudi Arabian peninsula, and southern Asia.

FUTURE WORK

This thesis has provided insight into the role of Fe chemistry in the atmosphere. However, much is still unknown about Fe and other transition metal chemistry in aerosol and cloudwater. The major challenge in this thesis was the difficulty associated with analyzing trace species in aerosol and cloudwater. Current spectrophotometric techniques used in this thesis for the quantification of Fe(II) and other trace metal oxidation states have serious limitations. These limitations include interferences with other aerosol and cloudwater chemical species, and sensitivity. Great care must be taken to eliminate the interferences or account for them. As for sensitivity, relatively large sample sizes must be collected for both aerosol and cloudwater in order to be in the range of the analytical technique. These large sample sizes ultimately require long sampling times, which are usually longer than the characteristic times associated with the reactions occurring in the aerosol or cloudwater system being sampled. Improved analytical and collection techniques which provide for the near real-time analysis of trace metal speciation in ambient aerosol and cloudwater systems would provide invaluable knowledge. Techniques, such as electro-spray mass spectrometry (ES-MS) show a great deal of promise, however their application to field studies is currently limited by the size and complexity of the instrumentation. And the problems associated with coupling an ES-MS instrument to a cloudwater collector are numerous.