

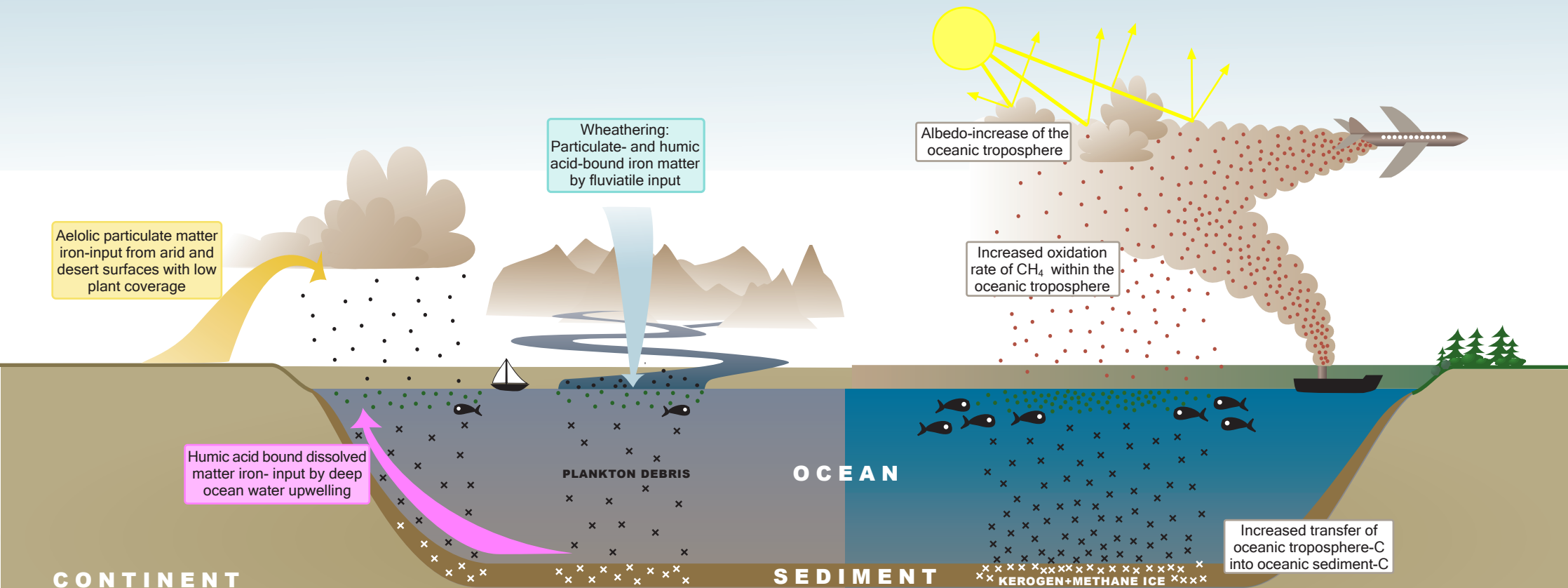
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# Climate Stabilization System by Metal Oxide Soot Enrichment of Tropospheric Volume Elements

Natural iron input into the ocean  
- inducing phyto plancton growth -

climate cooling by iron- and titanium oxide soot-enrichment of the  
troposphere along ship- and aircraft-trajectories induced by ship- and  
aircraft-fuel enrichment with metal-organic compounds



# Climate Stabilization System by Metal Oxide Soot Enrichment of Tropospheric Volume Elements

(international patents applied)

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## INTRODUCTION AND PROBLEM DESCRIPTION

In the continuing discussion over climate warming, it is unquestioned, that the increasing CO<sub>2</sub> level of the atmosphere owes a major share among the manifold factors responsible for this effect. The proposals at hand base on increasing the CO<sub>2</sub>-bonding in the oceanic sediments. Carbon is fixed therein in reduced form as bituminous and methane hydrate sediment on the ocean floor, or as carbonate in the warm and shallow regions. Sunlight along with phyto plankton serve to transform atmospheric CO<sub>2</sub> into sediment-bound reduced carbon (1). The conversion and transfer of the oxidized atmospheric carbon into reduced sediment carbon is performed by phytoplankton assimilation. Because iron is a very limited fertilizing element at the ocean surface, the hypothetical quantity of tropospheric CO<sub>2</sub>, transformable through a definite ocean surface area to phytoplankton depends on the availability of iron. It is known, that iron-containing dust originating from continental surfaces of low plant coverage, generated and transported by dust storms, sinking down to the ocean surface, may induce increase of carbon mass transfer (2, 3, 4). Other iron sources are upwelling cold deep-water and fluvial input of particles containing iron oxide minerals or bound to organic particles, colloids and dissolved matter of the humic acid type (picture 1). Increasing iron input may have been responsible for climate cooling during past geological episodes (6). Proven on bench-scale, one part of iron in the form of soluble salt into mid-oceanic surface water has the capacity to convert up to 10<sup>6</sup> parts of CO<sub>2</sub>-carbon into planktonic organic carbon (5). Field tests employing the propelling screws of vessels to distribute soluble iron salts have stimulated plankton blooms (5). However this method of mixing iron salt solutions into seawater differs greatly from that natural processes of iron enrichment of ocean areas; moreover, the iron solution mixing process holds disadvantages: the distribution of iron cannot be done in such manner, as would warrant an even concentration over large sea areas, and it is exclusively restricted to reduce the climate factor CO<sub>2</sub>. Aiming to operate closer to natural iron input processes proposals have been made to use artificial organic iron chelates (lignin acid sulfonate iron chelate) and to use floating organic pellets this iron complexes are fixed to preventing the iron compounds from fast leaving the uppermost phyto plankton rich ocean layer (60). But even these practices have not overcome said distribution problems.

Climate warming tends to self-accelerating. While rising temperatures cause the formerly to permanently frozen soil and ocean sediment bonded methane hydrate („methane ice”) to decompose to CH<sub>4</sub> rising up to the atmosphere. Sudden climate changes from cold to extremely warm climate in the course of past geological periods most probably had been triggered by events of CH<sub>4</sub>-emissions induced by rising temperatures (6, 43, 45). Similar mechanism seem to operate in the present: The atmospheric CO<sub>2</sub>- and CH<sub>4</sub>-levels are rapidly increasing (7). Other man made sources adding to the CH<sub>4</sub>-level are the extension of rice crops and fertilizer use (44). The global warming potential of CH<sub>4</sub> exceeds that of CO<sub>2</sub> by 21-fold. Yet the contemporary idea markets have not offered any recipe to reduce the global CH<sub>4</sub> level.

## PROBLEM SOLUTION

To successfully reproduce the climate cooling effects resulting from the episodes with increased natural iron entry into the oceans, state-of-the-art geo-engineering obliges as closely as possible to natural physical and chemical processing: low specific iron inputs per ocean surface unit from atmospheric iron sources of primary low dissolvability. Those claims have been made by environmental scientists (61). In pursue of this demand we propagate the enrichment of the tropospheric airspace covering the ocean with pigment soot composed of iron- and/or titanium-oxides. Both metal oxides are solid and are contained as well in solid natural aeolic and fluvial substance inputs into the oceans, although at much lower concentration in the solids. The atmospheric iron dust sources due to our proposal will establish at least one more advantages. This are the additional physical and

chemical tropospheric cooling mechanisms well known from natural dust inputs from the atmosphere. Due to the diameter of the primary soot particulates, which may be orders of magnitude smaller than that of natural atmospheric iron particles, particle residence period in the upper ocean layer will exceed the residence periods of natural particulate matter by far. This results in sustained fertilization of the plankton by undissolved particles at very low dissolved fertilizer concentration, avoiding fertilizer overdosage as well as any disordering of the plankton community composition, as suspected by environmental scientists if conventional ocean fertilization by iron salts should become common (61).

**Picture 1** displays a schematic description comparing essential natural iron entry processes into the ocean and resulting effects to those influences and results to be expected from the proposed artificial tropospheric distribution of pure iron- and/ or titanium-oxide pigment soot.

**Table 1** displays the variety of influences contributing to tropospheric climate cooling under utilization of the proposed tropospheric distribution of pure iron- and titanium-oxide pigment soot. Summarizing these effects, they may be split into three categories:

- a) climate cooling by increased oxidation rate of ocean troposphere CH<sub>4</sub>
- b) climate cooling by increased transfer rate of troposphere C into ocean sediment C
- c) climate cooling by increased albedo of ocean troposphere.

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The main advantage of our proposal is, that no additional technical equipment would be required to set it in practice. The only necessary measure is doping the fuels for trans oceanic aircrafts and ships by iron- and/or titanium organics. Fuel doping by metal organics aiming to optimize combustion processes is technical standard: iron organics reduce soot generation by heating oil combustion, manganese organics induce soot reduction in diesel engine exhaust gas and lead organics along with halogen organics improved octane value of gasoline.

**Tables 2 - 7 & Flowchart 1** describe the agents and reactions on and with the metal oxide soot pigments after releasing into the troposphere with the exhaust gases.

a) Reducing the atmosphere's CH<sub>4</sub>-level by increasing oxidation of CH<sub>4</sub>

The exhaust gases of engines combusting iron organics doped fuels carry solid residues consisting of an ultra-fine-grained red iron oxide soot pigment. Once released, the soot particles start to grow immediately due to well known mechanisms like adsorption, dissolution, absorption, agglomeration, photocatalytic activation, capillary condensation, chemical reaction and chemical and hygroscopic enrichment of water. The pigment particles' surface catalyzes exhaust gas- and atmospheric-originating sulfur compound oxidation like SO<sub>2</sub>, COS and dimethyl sulfide, so producing a liquid layer of sulfuric acid which reacts with and adheres to the pigment particles' surface. Additionally the pigment will collect organics, chloride, oxygen, ozone and nitrogenoxides, producing an effective oxidant mixture made of peroxides, halogens, halogenides, nitrous- and nitric-acid salts and, if irradiated by sunlight - quite a number of products resulting from photolytic reactions particularly hydroxyl- and chlorine-radicals (Tables 2 - 4). Once oxidants and reductants have built on the pigment particle surface, the result is a most reactive mixture. Compared to hydroxyl radicals, chlorine or chlorine radicals have proven most effective in the oxidation of CH<sub>4</sub>. Further fuel enrichment by chloro organics, sulfur or sulfur-organics will trigger the oxidant generating power of the iron oxide pigment soot.

Engines combusting titanium conditioned fuels release TiO<sub>2</sub> pigment soot. TiO<sub>2</sub>-pigments may possess strong photocatalytic power when exposed to sunlight: TiO<sub>2</sub> pigments will most probable produce more OH-radicals than 'virgin' iron oxide soot. Beyond, it is commonly known, that iron- or carbon-doped TiO<sub>2</sub>-pigments improves the power to generate oxidants when irradiated (8, 9, 10). Adequate fuel doped with iron- and titanium organics mixtures to generate iron doped TiO<sub>2</sub>-pigments and adequate oxygen-fuel combustion relations are proposed to generate carbon-doped TiO<sub>2</sub> soot pigments.

Both the hygroscopic- and adherant-character of liquid cover building on the pigment particle's surface and the catalytic and photocatalytic reactivity of its solid and liquid surface turn it into a pollutant scavenger which clears the atmosphere even from particulate matter, as is known from sea salt particles (40).

b) CO<sub>2</sub>-level reduction by plankton digestion of CO<sub>2</sub> into organic C and sedimentation

Unless the iron oxide soot released in the troposphere is not transported to the sea surface within short by rain or snow, it will float on for weeks with the wind until it sink down and reach the surface far from the location of release. During the extended dwelling period in the troposphere small parts of the primary iron oxide soot may turn into a soluble coating, which will not effect in disturbed plankton growth (61) upon contact with seawater. If practiced to the proposed extend and manner, a wide trace of blooming phyto plankton would visibly mark the courses of regular ship and aircraft crossings. Even if practiced for decades, environmental hazards incurred by an 'iron overdosage' may be excluded. The extremely small dimensions of possibly remaining undissolved iron oxide soot particles float long enough in the uppermost seawater layer to be completely 'digested' by plankton, while coarse grained natural iron bearing particulate matter (e.g. loess, volcanic ash, desert dust - an exclusion may be space dust) will have shorter residence within the uppermost seawater layer and at least parts of the iron content is hidden and inaccessible.

Iron stimulates the microbes' production of the plankton fertilizer nitrate (41). Thus even in oceanic ranges of dense natural plankton population, the propagated addition of iron oxide soot pigment will prompt additional plankton growth. Most effective oceanic areas to sequester carbon by iron oxide soot fertilization are those containing oxygen only in a ocean surface layer. This conditions are known to exist in the Black Sea.

As an additional positive side effect the plankton growth stimulation offers a viable chance to increase the marine food production, because plankton represents the most important link of the oceanic food chain. Titanium- and iron-oxide pigment soot tends to adhere to oil- and bituminous residues floating on the sea around ship tracks, as well as plastic trash, upon which chemical, photochemical, and biochemical reactions accelerate mineralization and humification of the pollutants.

c) Increasing the planet's albedo lowers troposphere's temperature

Low rating of iron- and/or titanium organic fuel additives even may decrease the particle quantity of particles contained in the exhaust gas, because the metal oxides catalyze combustion of the carbon soot particle fraction and by that, will reduce total soot particle content within the exhaust gas. The black carbon soot particles' capacity to absorb light would considerably contribute to warm the surrounding atmosphere (38, 42). In reversal, the prevention of carbon soot prompts a cooling effect. Compared to carbon soot, mineral aerosol particles show only negligibly low light absorption quantity and are light reflectors. Mineral particle haze induces a cooling effect (42). Correspondingly the release of haze, composed of iron- and/or titanium-oxide pigment soot will prompt a cooling effect in the troposphere.

Another very positive secondary effect accompanying the increase of the plankton mass is the rise in secretion of organic sulfur, particularly dimethylsulfide (DMS). Catalyzing the mineralization of DMS to liquid sulfuric acid, surrounding iron- and/or titanium-oxide soot pigments prompts increase in cloud creation. Increased cloud coverage cools the troposphere because of increased albedo. The well known effect of producing denser and „whiter“ clouds by high concentrations of microparticulate matter may induce an additional albedo increase. At certain circumstances artificial aerosols might suppress snow and rain precipitation (39). But those effects may be compensated within the lower oceanic troposphere where the sea salt particulate haze may compensate this effect (40).

## PERSPECTIVES

Project funding for introduction and operation of proposed climate stabilizing system by pigment enrichment of the oceanic troposphere will be activated as soon as adequate world wide emission trade systems will have come into action or when CO<sub>2</sub> emissions will have become taxable. Regulations aiming to install such emission trade systems are in preparation or even in action (e.g. EU Emission Trade System Directive 2003/87/EC). When those emission trade- or tax systems will be in effect, even at iron- or titanium-contents in the combusted fuel as low as just sufficient to return only the fuel carbon mass equivalent combusted,

1. into ocean sediment and/or
2. mineralizing 0,05 parts of tropospheric CH<sub>4</sub>-Carbon mass equivalent per combusted fuel carbon

mass equivalent,

fuel doping with iron- and/or titanium-organics should be operable without any additional cost: because fuel combustion at this dopant concentration, unless the fuel quantity combusted, will not add any greenhouse equivalent to the global CO<sub>2</sub>- and CH<sub>4</sub>-budget. Increased fuel dopant concentrations result in exceeding the carbon mass equivalent combusted by said CO<sub>2</sub> carbon mass equivalents transferred into sediment and of CH<sub>4</sub>-carbon mass equivalents mineralized, the resulting exceeding carbon mass transfers reducing atmospheric CO<sub>2</sub>- and CH<sub>4</sub>-budget are tradable at stock exchanges.

The propable partners to join in realization of the recommended climate cooling project (financing, supporting, testing and using) are governments, shipping companies, airlines, oil companies and chemical companies as producers or potential producers of iron- and titanium organics.

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### Tropospheric growth mechanisms of ship- and aircraft-generated Fe- and Ti-oxide soot pigment particles

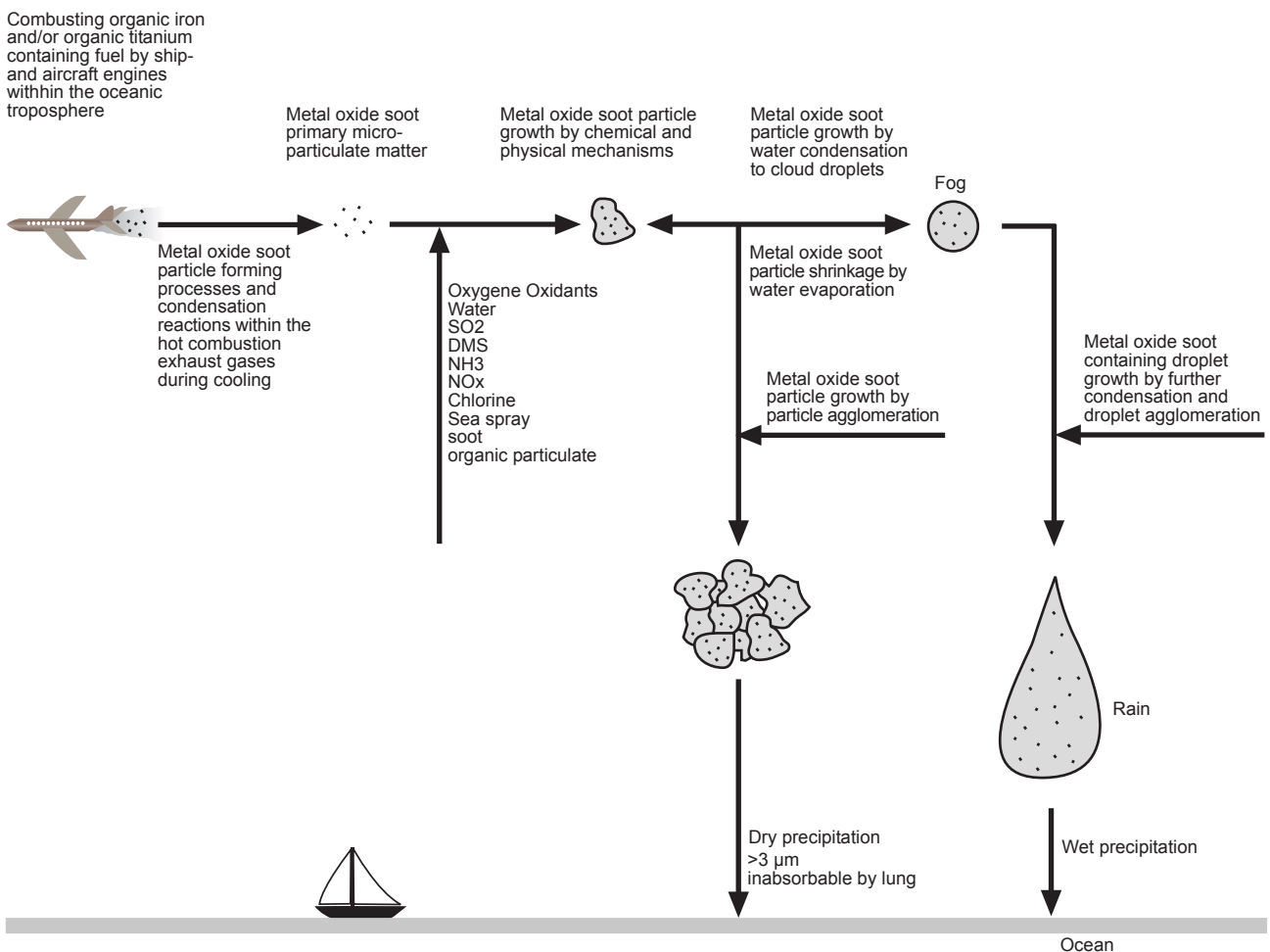


Table 1

| Climate cooling effects induced by the enrichment of ship- and aircraft-fuels with iron- and titanium-organics   |
|--|
| Methane oxidation by enrichment of the oceanic troposphere with chlorine-and hydroxyl-radical oxidants   |
| Increasing the oceanic albedo by light reflection on the metal oxide soot pigment haze induced by the pigment enriched exhaust gases   |
| Increasing the albedo by sulfuric acid bearing metal oxide soot pigment induced dense clouds   |
| Increasing the albedo by preventing black carbon soot generation during fuel combustion by metal oxide soot  |
| Increasing the albedo by triggering the chain: increasing DMS-production by iron oxide soot pigment fertilization of phytoplankton, conversion of DMS on iron oxide soot pigment to sulfuric acid acting as cloud condensing aid |
| Increasing the transfer of tropospheric carbon dioxide carbon into methane ice- and kerogen-carbon sediment by increasing phytoplankton carbon mass of phytoplankton debris carbon mass sedimentation                            |

Table 2

| Expected factors influencing particle growth by substance addition to the pigment particles during their tropospheric residence period |   |
|--|---|
| <b>Substance addition to the soot pigment particle, expected substance species</b>   | <b>Conditions influencing tropospheric species concentration or species addition to the soot pigment particle</b> |
| Water  | relative humidity   |
| Oxygen   | -   |
| Nitrogenoxides   | traffic emissions   |
| Nitrous acid (16)  | traffic emissions & sunshine  |
| Nitric acid (20, 22)   | traffic emissions & sunshine  |
| Ozone (34)   | diff. man made emiss. & sunshine  |
| Hydrogen peroxide (24)   | diff. man made emiss. & sunshine  |
| Chlorine (15, 17, 20, 36, 37)  | sunshine  |
| Bromine (33)   | sunshine & plankton fertilization   |
| Jodine (35)  | plankton fertilization  |
| Dimethylsulfide (11, 23)   | plankton fertilization  |
| Dimethylsulphoniopropionate (11)   | plankton fertilization  |
| Sulfur dioxide (21)  | traffic emissions   |
| Carbonylsulfide (21)   | -   |
| Methane (24)   | -   |
| Volatile organic compounds (12, 14)  | different urban emissions   |
| Sulfuric acid (13)   | traffic emissions & plankton fertil.  |
| Ammonia (13)   | -   |
| Hydrogen chloride (15)   | sunshine  |
| Seasalt particulate matter (17)  | hight above sealevel  |
| Organic aerosols (19)  | different urban emissions   |
| Soot particulate matter  | different urban emissions   |
| Ultrafine particulate matter of the upper troposphere (18)   | -   |

Table 5

| Expected main components of the liquid and/or solid layers on titanium oxide soot pigment particle surfaces after weathering during oceanic tropospheric residence period |                                     |
|---|-------------------------------------|
| <b>Liquid phase</b>   | <b>Solid phase</b>                  |
| Water   | Water                               |
| Sulfuric acid   | Ammonium sulfate                    |
| Ammonium sulfate  | Ammonium nitrate                    |
| Ammonium nitrate  | Sodium sulfate                      |
| Sodium sulfate  | Sodium nitrate                      |
| Sodium nitrate  | Sodium chloride                     |
| Sodium chloride   | Titanium oxidhydrates               |
|   | Oxidized organic particulate matter |
|   | Oxidized carbon soot                |

Table 6

| Expected main components of the liquid and/or solid layers on iron oxide soot pigment particle surfaces after weathering during oceanic tropospheric residence period |                    |
|---|--------------------|
| <b>Liquid phase</b>   | <b>Solid phase</b> |
| Water   | Water              |
| Sulfuric acid   | Ammonium sulfate   |
| Ammonium sulfate  | Sodium sulfate     |
| Ammonium nitrate  | Sodium nitrate     |
| Sodium sulfate  | Sodium chloride    |
| Sodium nitrate  | Iron(III) sulfate  |
| Sodium chloride   | Iron(III) nitrate  |
| Iron(III) sulfate   | Iron(III) chloride |
| Iron(III) nitrate   | Iron(II) chloride  |
| Iron(III) chloride  |                    |
| Iron(II) chloride   |                    |

Table 3

| Expected chemical reactions on dry and wet iron oxide soot pigment particle surfaces during their tropospheric residence period |
|---|
| Oxidation of chloride ion by NO2+ to ClNO2 (29, 31)   |
| Photolytic decomposition of ClNO2 to Chlorine Radicals and NO2 (31)   |
| Oxidation of chloride ion by NO3 to Chlorine (30)   |
| Oxidation of incomplete oxidized iron to iron(III) oxide hydrates   |
| Hydrolysis of N2O5 to nitric acid (32)  |
| Hydrolyzation of hematitic iron to iron(III) oxide hydrates   |
| Hydrolyzation of dissolved iron(III) compounds to iron(III) oxide hydrates  |
| Catalytic oxidation of sulfur compounds to iron(III) sulfate (59)   |
| Dissolution of pigment surface by sulfuric acid   |
| Oxidation of iron(II) compounds by hydrogen peroxide to iron(III)compounds and hydroxyl radical (28)                            |
| Oxidation of iron(II) compounds by dioxygenanions to iron(III)compounds and hydrogen peroxide (25, 49)                          |
| Oxidation of iron(II) compounds by chlorine to iron(III)compounds   |
| Oxidation of iron(II) compounds by ozone to iron(III)compounds  |
| Photocatalytic decomposition of iron(III)chloride to iron(II)chlorid and chlorine (light reaction)(26)                          |
| Photocatalytic decomposition of iron(III) organics to iron(II) organics and organic radical (light reaction) (27)               |
| Photocatalytic decomposition of iron(III)nitrate to iron(II)nitrate, nitrogenoxides and OH-radicals (light reaction)            |
| Photocatalytic decomposition of iron(III)sulfate to iron(II)sulfate and hydroxyl radicals (light reaction)                      |
| Ozone decomposition to Oxygen, hydroxylradicals and hydrogen peroxide (dark and light reaction)                                 |
| Methane oxidation to carbondioxide and water by chlorine and/or hydroxyl radicals (24)  |

Table 4

| Expected reactions of dry and wet titanium oxide soot pigment particle surfaces during their tropospheric residence period      |
|---|
| Hydrolyzation of titanium oxides to titanium oxide hydrates   |
| Photolytic production of hydroxyl radicals by titanium dioxide (36, 46, 47, 48)   |
| Photocatalytic oxidation of adhering organic material on titanium dioxide (50)  |
| Photocatalytic oxidation of organic material on titanium dioxide with hydrogen peroxide as by-product (52)                      |
| Photocatalytic oxidation of halogen organic material on titanium dioxide (51, 53, 56, 58)                                       |
| Photocatalytic oxidation of sulfur organics, ammonia and hydrogensulfide on titanium dioxide (57)                               |
| Photocatalytic oxidation of organic material on titanium dioxide in the presence of iron salts (10)                             |
| Photocatalytic oxidation of organic material on particle mixtures containing titaniumdioxide- and iron(III)oxide-particles (54) |
| Photocatalytic oxidation of NO and NO2 to HNO3 by TiO2- activated carbon- and iron(III)oxide-powder mixture (55)                |
| Photocatalytic oxidation of organic material on titaniumdioxide particles doted with iron (8)                                   |
| Photocatalytic oxidation of organic material on titaniumdioxide particles doted with carbon (9)                                 |
| Photocatalytic seasalt conversion by oxidation of chloride to chlorine  |
| Photocatalytic oxidation of methane in the presence of sea salt by chlorine   |

Table 7

| Mechanisms controlling soot particle growth during oceanic tropospheric residence period |                           |
|--|---------------------------|
| <b>Chemical mechanisms</b>   | <b>Physical mechnisms</b> |
| Chemical reaction  | Capillary condensation    |
| Photo chemical reaction  | Condensation              |
| Dissolution  | Dissolution               |
| Absorption   | Adsorption                |
| Hygroscopicity   | Absorption                |
| Precipitation  | Hygroscopicity            |
|  | Spray electrification     |
|  | Particle electrification  |
|  | Adhesion                  |
|  | Attraction                |
|  | Repulsion                 |
|  | Evaporation               |
|  | Crystallization           |



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