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#### Protection of the oceans by patented climate cooling

The growth of the world population is associated with an increase in incineration processes. Combustions are greenhouse gas emitters and known as main producers of the climate warming problem. Knowing about these fateful facts we worked out the ISA refrigeration procedure: One of the main essentials of the ISA (Iron **S**alt **A**erosol) procedure is the instrumentation of the combustion processes as climate cooling and greenhouse gas destruction processes.

According to the IPCC report 5, which was released in November 2014, in fact global warming proceeds. Climate warming changes the continental and marine ecosystems. Recently, the risk was recognized that as a result of global warming, the vertical mixing in the oceans gets limited and can even completely reach a stagnation point (de Lavergne et al. 2014, Bernardello et al. 2014a and 2014b).

In consequence the oxygen supply is reduced or interrupted in the depths of the ocean. Already in present the formation of low-oxygen areas in the oceans increases (Capone & Hutchins 2013, Kalvelage et al. 2013). In particular, the climate warming-induced heating of the upper water layer weakens the thermohaline circulation by promoting the density stratification. This triggers the formation of oxygen-depleted zones (Voss et al. 2013).

Warm surface waters and decreasing input of cold oxygenated surface water triggers a temperature rise of the sediments, transforming solid methane hydrate to gaseous methane emission into the seawater (Phrampus et al. 2014). Methane oxidation consumes additional oxygen, decreasing the oxygen content above those areas (Yamamoto et al. 2014).

These facts have the threatening consequence of a sprawling lack of oxygen in the oceans. In the low-oxygen areas only bacterial life is possible, higher life forms do not exist there. Accordingly, very early result of the climate warming progression will be the dramatic limitation of the food source ocean.

Only the complete STOP of the global warming and the return to a normal climate can prevent a further growing of that alarming scale. As the only realistic chance of averting this development, we see the controlled application of that climate cooling process, the nature has used in the last ice age several times with high efficiency.

Meanwhile its undoubted clear that the natural process, that has caused the cold periods, has been triggered by the iron content in the mineral dust known as loess after sedimentation: The iron fraction of wind-blown dust aerosol fertilized the oceans phytoplankton and where sparking its enormous increase by assimilative conversion of  $CO_2$  carbon into organic carbon (Martin, 1990, Martinez-Garcia et al. 2011, 2014). But the only effective refrigerant within this process stage is the small content of water-soluble iron salt in the dust particles which triggers this fertilization effect (Duggen et al. 1977). By influence of the sun's radiation the primary insoluble iron fraction of the dust aerosol is transformed into the soluble iron salt aerosol (Johnson & Meskhidze 2013).

The cooling dust concentration in the troposphere increased during every cold period in the Ice Age to a multiple of today (Martinez-Garcia et al. 2011, Lamy et al. 2014), letting decrease the average temperature respectively up to 10 °C. The loess sediments in the northern and southern hemisphere on continents and ocean floors originate from these cold periods.

This natural dust process counteracts the climate warming. We instrumentalized this process creating the ISA refrigeration procedure. The ISA procedure is the much more effective, controllable and economic counterpart of the natural dust refrigeration process. Because it has the same physical, chemical and biological basement like the natural dust process the ISA procedure may be designated a nature-identical refrigeration process.

Adapted to the location and available technology, we have developed three ISA emission methods to accomplish the ISA refrigeration procedure from moving or stationary systems:

• Method 1: Pure iron oxide dust emission into the Troposphere by combustion of ironorganic additives in fuels and heating oils in ship and and jet motors or in power stations. Useful side effects of these additives are optimizing the fuel efficiency and minimizing the soot emission. Comparing to the natural iron oxide minerals the conversion of the emitted iron oxide aerosol into the ISA refrigerant happens several times faster comparing to the iron oxide minerals in the natural loess dust particles.

• Method 2: Emission of gaseous iron (III) chloride. When entering the atmosphere it converts directly into ISA refrigerant.

• Method 3: Direct ISA refrigerant emission. ISA is produced by the nebulization of aqueous iron(III) salt solution.

The ISA refrigeration begins in the atmosphere with some effects out of a multi-stage refrigeration process cascade. Each of the ISA refrigeration process stages unfolds a climate-cooling potential for itself: The process steps occur in the troposphere (1, 2, 3, 5) in the ocean (4, 6) and in the oceanic sediment (7, 8, 9). The nine main steps of this process cascade are described as follows:

#### 1. Troposphere:

Hygroscopic salt aerosols act as cloud condensation nuclei (CCN) (Karydis et al 2013, Levine et al., 2005.). ISA particles have same characteristics. According to Rosenfeld & Freud (2011) high CCN particle concentrations have different cooling effects. Each effect triggers the refrigeration by a separate reflectance (albedo) increase:

• Cloud formation even at low super saturation

• Formation of very small cloud droplets at an elevated number of droplets per volume. This causes a higher whiteness of clouds

• Extending the lifetime of clouds as the small cloud droplets cannot coagulate with each other. The precipitation from these clouds can only happen through snow crystal formation.

#### 2. Troposphere:

By sunlight photo-reduction of Fe(III) to Fe(II) in the salty maritime atmosphere the ISA refrigerant releases chlorine radicals (Wittmer et al. 2014a and 2014b). This oxidant reacts with the greenhouse gas methane 16 times faster than the hydroxyl radicals of the ISA-free atmosphere. The reaction product HCl combines with the iron oxide aerosol triggering the ISA production. In a second day time independent reaction reaction the ISA refrigerant catalyzes the formation of chlorine from chloride by tropospheric ozone (Sadanaga et al., 2012). Both chlorine-triggered methane decompositions cool the troposphere. Indications are known that this reactions where active during the glacial period: Levine et al. (2011) found elevated <sup>13</sup>CH<sub>4</sub> / <sup>12</sup>CH<sub>4</sub> isotope ratios in those Antarctic ice core segments representing cold glacial periods. The much greater chlorine preference for <sup>12</sup>CH<sub>4</sub> oxidation than that of the <sup>13</sup>CH<sub>4</sub> oxidation by the hydroxyl radical is the explanation for this unusual isotope ratio. Additional proofs are the deeply lowered methane concentrations during the hydroxyl radical periods.

#### 3. Troposphere:

The oxidation of black and brown carbon from natural but mostly man-made combustion processes causes the degradation of their water repellency and makes them hydrophilic. The hydrophilic carbon particles are washed out of the atmosphere by precipitation (Zuberi et al. 2005). The ISA refrigerant accelerates this oxidation process because the iron-induced Fenton and photo-Fenton reaction cycles produce hydroxyl and chlorine radical oxidants speeding up the soot oxidation. Shortening the soot lifetime in the troposphere has a cooling effect.

#### 4. Ocean:

The phytoplankton growth in the oceans is inhibited by the prevailing iron deficiency. Therefore the ISA-containing precipitation fertilizes the phytoplankton. This triggers the phytoplankton reproduction increasing the formation of organic carbon from the greenhouse gas  $CO_2$  (Martinez-Garcia et al. 2014). The vast majority of the thus formed only slightly water soluble oxygen (11 mg  $O_2$  / I) escapes into the atmosphere. In contrast, the formed organic carbon remains completely back in the ocean as the basis of the marine food and debris chain. This removal increase of the greenhouse gas  $CO_2$  cools the troposphere. Also during the ice age, this process has worked, as the evaluations of Antarctic ice cores show: During the high dust phases far lowered  $CO_2$  concentrations and temperatures in the troposphere were present (Skinner, 2008).

#### 5. Troposphere:

One consequence of the ISA-induced phytoplankton growth is the corresponding increase in the emission of dimethylsulfide (DMS) to the troposphere. DMS is an essential oil that is released from phytoplankton. It is reacting in the troposphere to sulfate and sulfonate aerosol, highly active cloud condensation nuclei (CCN). This process enhances the direct ISA cooling effect according to Process Step 1 (Charlson et al. 1987).

#### 6. Ocean:

The ocean ecosystem is based on the balance between oxidizing and reducing agents. As a result of the ISA refrigerant triggered additional input of organic carbon in the ISA immission region, according to process stage 4, under it in the water column local oxygen consumption can increase.

But today even without ISA influence, oxygen deficiency has been formed in many parts of the ocean. Its formation is usually less the result of increased phytoplankton production, but small vertical water exchange owed by increased vertical density gradient. Oxygen deficiency is found frequently between the oxic surface layer and the oxic deep water layer (Bruland 2006 Capone & Hutchins, 2013). Due to the climate warming the lack of oxygen zones does intensify and expand already today (Capone & Hutchins, 2013, Kalvelage et al. 2013).

With the ISA induced cooling the oxygen content of the deep ocean basins increases by growing input of the cold dense oxygen-enriched polar surface water. Reduced melt water production within the polar hemispheres and falling surface layer temperatures restore and intensify the thermohaline circulation within the northern polar regions and growing circum Antarctic sea ice cover induce production of cold high density brines sinking to the ocean basin bottoms. (Rahmstorf 2006, Ohshima et al. 2013).

#### 7. Sediment:

By influence of increasing organic content in the sediment under the ISA immission area therein constitutes suboxic to anoxic milieu resulting in the reduction of nitrate and sulfate as well as the solid oxides of Fe(III) and Mn(III) and Mn(IV) (Wallmann et al. 2008, Öhman et al. 1991, Swanson 1988). This microbe-induced metabolism mobilize fertilizers out of the sediment: Ammonium, phosphate, Fe(II), Mn(II) and silicon as organic complexes. Suboxic sediments are the best iron(II) emitters but even in anoxic sediments elevated iron solubility is found (Rickard, 2006).

The sediment overlying ocean bottom water layer accumulates this fertilizing solution from the sediments. Via the ocean current system the fertilizing potential reach the upper water cycle followed by fertilizing the phytoplankton and activating its reproduction. This as well triggers the CO<sub>2</sub>-conversion to organic carbon resulting in cooling the troposphere

according to step 4. Repeatedly it also cools the troposphere by increasing the DMS formation according to step 5.

#### 8. Sediment:

As mentioned in step 7, the biological processes of chemical sediment reduction induced by the ISA fertilization change nitrate, sulfate, Fe(III), Mn(III/IV)and hydrogen carbonate to their deoxygenated and reduced species inclusive methane and ammonium. This reduction chemistry is accompanied by pH change to alkaline. This alkalization accompanied by microbe metabolisms convert dissolved  $HCO_3^-$  into solid lime and dolomite (Krause et al. 2012, Raiswell & Fisher 2004, Luff & Wallmann 2003, Berner et al. 1970). The carbonate precipitates stabilize the sediment. The carbonate precipitation fixes additional parts of  $CO_2$ , prevents the ocean water from acidifying and improves the  $CO_2$  absorption by ocean water from the atmosphere. This again cools the troposphere.

#### 9. Sediment:

Anoxic sediments outside the methane hydrate stable pressure and temperature region induce deoxygenation within the overlying water layer by methane emission (Yamamoto et al. 2014, Römer et al. 2014). Methane emissions are induced for instance by hydrothermal springs (Suess 1999), sediment movement (Krastel et al. 2014, Paull et al. 2007), climate change induced seawater warming (Shakova et al. 2005, Fulton-Bennet 2007/2012), changing ocean circulation (Berndt et al. 2014), ocean sediment subduction (Fischer et al. 2013, Elvert et al. 2000). Often the methane emissions reach the troposphere. Because the Arctic Ocean suffers at most from the climate change induced warming the methane release within this region rise extraordinary (Phrampus et al. 2014). The most elevated Global methane concentrations are located within the Arctic Ocean and the arctic troposphere (Shakova et al. 2008). This is one of the reasons for the extraordinary temperature rise of the arctic region.

Within the sediment and within the suboxic ocean water column methane is oxidized by sulfate. Iron is an accelerator of this microbial fermentation reaction (Sivan et al. 2014). The ocean water column and the underlying sediment having had contact with ISA-originating iron are elevated in their iron content. This has different cooling effects to the troposphere: At first the elevated iron content reduces the methane content emitted by the sediment. Next the iron content reduces the methane bubble-development within the sediment layer preventing catastrophic methane eruptions by sediment destabilization, methane bursts and sediment avalanches. Third: Preventing the ocean from methane-induced oxygen deficiency by elevated iron content prevents from the formation of ammonium within the water column. Side product of the ammonium fermentation by oxygen is the extreme stable and very effective greenhouse gas  $N_2O$  (Naqvi et al. 2010).

The actual input of iron from the atmosphere in the form of soluble salt is calculated to 100000 up to 260000 t per year (Myriokefalitakis et al. 2014, Johnson & Meskhidze 2013). A size of a sustaining ISA refrigerant emission between this and the next lower order of magnitude seems to fit a realistic economy order to become realized by mankind over couples of decades.

By reference to the iron salt induced ice age cooling processes: Nature directed her cooling course in close analogy to the ISA refrigeration procedure by enormous dust concentrations and dropped the climate temperatures up to 10 °C. Today it needs a mean global temperature drop of only 0.5 to 1 °C to normalize the mean global temperatures. But for sustaining survival of mankind it is necessary to restore and save the oceans food web immediately. The only possibility to do that is the immediate return to climate normality. The only way to do this without irreversible damage to the ecosystems of the planet is starting to practice the ISA refrigeration procedure. The ISA procedure is the first climate cooling method which has proved its effectivity: The ISA methods multiple prove are the lots of dust cooled ages during the glacial time.

As documented in this paper the very different ISA cooling mechanisms are decoded now – at last during this year: The tropospheric methane elimination chemistry by the ISA refrigeration procedure has been decoded by the scientist team of the Research Laboratory for Atmospheric Chemistry at the University of Bayreuth. Their results will soon be published in a well-known scientific paper.

## The effectivity of the ISA refrigeration procedure for climate cooling has been proved in detail. It is an effectivity-optimized variant of its corresponding natural process.

All other known proposals to cool the climate seem disadvantageous comparing to the ISA method, because their cooling effects are mono-causal and without any proof. Additional they have no proof that they do no harm to the environment.

# The ISA climate cooling opens a nearly free of charge possibility to repair climate warming induced manifest harms and damages without the need to stop the continuing use of fossile carbon resources.

The global fixing regulation of the greenhouse gas emission certificate price values and the ISA emission certificate credit values would be a simple but effective measure for the quickest world-wide implementation of the ISA-Method.

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