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(54) Title: METHOD FOR SELECTION OF APPROPRIATE LOCATION TO REDUCE THE ATMOSPHERIC CARBON DIOX-
IDE THROUGH LARGE-SCALE IRON FERTILIZATION WITH LESS ACCUMULATION RATE OF VOLCANIC SULFUR
COMPOUNDS

(57) Abstract:



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Description

Title of Invention: METHOD FOR SELECTION OF APPROPRIATE LOCATION TO REDUCE THE ATMOSPHERIC CARBON DIOXIDE THROUGH LARGE-SCALE IRON FERTILIZATION WITH LESS ACCUMULATION RATE OF VOLCANIC SULFUR COMPOUNDS

Technical Field

- [1] The present method is related to the appropriate location for the large-scale sequestration of the atmospheric carbon dioxide. It is well-known that such a carbon dioxide is the main reason of the recent climate change. Many investigators have attempted internationally to resolve the problem of temperature increase caused by the enormous fuel combustion. Ever since John Martin proposed the iron hypothesis in 1988 to reduce the atmospheric CO₂, 14 mesoscale iron fertilization experiments have been carried out in HNLC regions until 2012. However, none has yet demonstrated economically feasible results so far. As pointed out by Boyd in 2005, the right choice for the location of future experiment is so important to be successful in the atmospheric CO₂ sequestration. The present method shows the details in regard to the selection of appropriate location to reduce the atmospheric CO₂ through the large-scale iron fertilization with the scopes of 5W1H (Who, When, Where, What, Why, How)

Background Art

- [2] The recent necessity of sequestering atmospheric CO₂ produced enormously by fossil fuel combustion to be within the emission standards set up by the 2005 Kyoto Protocol to the United Nations Framework Convention on Climate Change, ever since several countries and the European Union have established carbon offset markets which trade certified emission reduction credits (CERs) and other types of carbon credit instrument internationally.
- [3] The hypothesis of iron fertilization was speculated by English biologist Joseph Hart in 1934, raised by John Gribbin in 1988, and renewed by American oceanographer John Martin four months later. As reviewed by Dugdale and Wilkerson, Barber and Ryther described an area of east of the Galapagos Islands in 1969 and Strickland et al. had interests in waters exhibiting relatively abundant nutrients, but low chlorophyll and low productivity in 1969. Minas et al. has firstly designated the terms of "high nutrient, low chlorophyll (HNLC)" in 1986. Martin's iron enrichment experiments into the amounts of carbon drawn into the seas by algae formed the basis for 14 mesoscale international efforts during the last 20 years to understand the ocean's role in the Earth's

carbon budget. However, none has yet demonstrated economically feasible results so far. Therefore, further modification of such experimental protocols should be scientifically developed so that Martin's hypothesis come true in large scale. 14 mesoscale iron enrichment experiments have been carried out at southern Africa, Australia, and New Zealand of the Southern Ocean with the Equatorial Pacific and the Subarctic Pacific. As pointed out by Boyd in 2005, the right choice for the location of future experiment is so important to be successful in the atmospheric CO₂ sequestration.

- [4] In most regions of the world ocean photosynthetic production is limited by the availability of the nutrients nitrate and phosphates. Regions where nutrients concentrations are high, are usually characterized by high concentrations of chlorophyll in surface waters. There are, however, large areas of the world ocean(>30%) where the concentrations of nutrients are high yet chlorophyll is low (that is, high-nutrient-low-chlorophyll (HNLC) waters). Martin and Fitzwater hypothesized in 1988 that primary productivity in HNLC regions was limited by the availability of iron while HNLC regions consist of the Subarctic Pacific, Equatorial Pacific, and Southern Ocean, as illustrated in Table 1. Deposition of iron to these regions also has important implications for the CO₂ sequestration, as increases in iron to the oceans may result in increased phytoplankton growth and hence a decrease of CO₂ in the atmosphere (Mahowald et al., 2005).

- [5] Table 1

[Table 1]

HNLC	Nitrate(μM)	Phosphate(μM)	Silicate(μM)	Chlorophyll-a ($\mu\text{g l}^{-1}$)	Aeolian dust(Tan, 2013) ($\text{g m}^{-2}\text{yr}^{-1}$)
Southern Ocean(Scotia Sea)(Dugdale and Wilkerson, 1991)	31	3.4	32	2.2	4
Equatorial Pacific(Dugdale and Wilkerson, 1991)	7	1.0	3	0.3	7
Subarctic Pacific(Tan et al., 2013)	10.97	1.17	23.18	0.72	14

[6] Table 1. Distribution of nutrients, chlorophyll and aeolian dust in HNLC regions.

[7]

[8] Iron is an important limiting nutrient for algae, which use it to produce chlorophyll and protein. Photosynthesis depends on adequate iron supply, whose concentration in water is quite low because of its low solubility. The primary producers in the ocean that absorb iron are typically phytoplankton or cyanobacteria. Iron is then assimilated by consumers when they eat the bacteria or plankton, the latter providing a crucial source of food to many large aquatic organisms such as fish and whales. When animals, fishes and plankton die, decomposing bacteria return iron to the soil and the water.

[9] Hematite(Fe_2O_3) and goethite(FeOOH) in the aeolian dust tend to be associated with fine($0.3\sim 1\mu\text{m}$) particles, with long residence times(days) in the atmosphere and thus potentially long transport paths(Maher et al., 2010).

[10] Under oxic conditions typifying surface waters, Fe exists largely in the oxidized ferric (Fe^{3+}) form; as insoluble oxides, hydroxides, and carbonates which readily precipitate and deposit in the sediments. Under anoxic conditions, Fe may be released from the sediments as more available reduced Fe^{2+} prior to algal blooms, as shown

stepwisely in Fig. 1.

- [11] Since the solubility of N_2 is very low in comparison with those of CO_2 (high), PO_4^{3-} (moderate), and SO_2 (very high), the overall algal growth rate is governed by the rate of N assimilation and N_2 fixation, requiring a plenty of iron atoms. The Subarctic and Equatorial Pacific and the Southern Ocean surrounding the Antarctic, are collectively known as "high nutrient - low chlorophyll" (HNLC) regions. This is because HNLC algal populations are surprisingly low, considering the relatively high availability of most mineral nutrients there. In HNLC regions extremely low levels of dissolved iron (0.000004ppm) (Boyd et al., 2001) explain the low algal productivity. However, *Synechococcus* reached high densities in most HNLC regions. This may be caused by its ability to synthesize siderophores, iron-binding compounds, which facilitated the transport of iron ion into cells within 2 hours (Walsh and Steidinger, 2001) during periods of iron deficiency. Iron is an enzyme cofactor in numerous biochemical pathways. Specifically, enzymes involved in photosynthesis, electron transport, energy transfer, N (specifically nitrate and nitrite) assimilation, and (in the case of cyanobacteria) N_2 fixation require iron. In nitrogen-fixing cells, each nitrogenase complex contains 32 to 36 iron atoms (Graham et al., 2009). Photosynthetic cells require relatively large amounts of iron for photosystem reaction centers. Photosynthesis takes place in chloroplast to capture light energy, whose principal photoreceptor is chlorophyll-a with molecular formula of $C_{55}H_{68}O_5N_4Mg$. The number of nitrogen atom is thus four per molecule of chlorophyll-a, which requires four NH_4^+ ions to be synthesized to chlorophyll by nitrogenase complex. Since 14 iron atoms are necessary during the process of photosystem I and 32 to 36 iron atoms are contained in nitrogenase complex during N_2 fixation, and thus, $(14 \times 4) + (32 \sim 36) = 88 \sim 92$ iron atoms can be minimally necessary for the biosynthesis of a molecule of chlorophyll-a. Each photosynthetic cell contains 40~200 chloroplasts while each chloroplast has grana containing 10~20 thylakoid and thylakoid membrane is covered with 300 chlorophylls (Lewis et al., 2009). It is thus expected that each photosynthetic cell contains $1.2 \times 10^5 \sim 1.2 \times 10^6$ chlorophylls to be approximated that each photosynthetic cell of algae requires iron atoms as much as : $(88 \sim 92 \text{ iron atoms/chlorophyll-a}) \times (1.2 \times 10^5 \sim 1.2 \times 10^6 \text{ chlorophyll-a /algae cell}) = 1 \times 10^7 \sim 1 \times 10^8 \text{ iron atoms/algae cell}$, which can be close to the experimental observation of intracellular iron quota (Henley and Yin, 1998) for *Synechococcus* spp. of $\sim 10^{-18} \text{ mol/cell}$ ($\sim 1 \times 10^6 \text{ iron atoms/cell}$). Since the algal concentration is in the range of 10^6 cells/ml during algal blooms (Ahn et al., 2004), the resultant iron atom concentration can be $1 \times 10^{13} \sim 1 \times 10^{14} \text{ iron atoms/ml}$. If blooming patch is assumed to have 100 meter long, 100 meter wide and 1 meter deep during photosynthesis, its volume can be $10^4 m^3$ or 10^7 liter . Thus, the required iron atoms in such a volume can be $1 \times 10^{23} \sim 1 \times 10^{24} \text{ iron atoms}$ during algal blooms. Besides, one

mole of iron is 55.8g with 6×10^{23} atoms, the corresponding iron concentration is 0.001~0.01ppm $\left\{ \frac{(1 \times 10^{23} \text{ } 1 \times 10^{24})(55.8 \times 10^3 \text{ mg})}{(6 \times 10^{23})(10^7 \text{ l})} \right\}$, which can be comparable to

0.0034ppm in seawater and 0.3ppm in drinking water. It is thus expected that iron ion in either seawater or freshwater can be minimally satisfied to synthesize only chlorophyll-a containing algae cell although much more iron can be required further for protein and cellular reproduction during algal blooms, as conceptually shown in Fig. 2.

[12]

Disclosure of Invention

Technical Problem

[13] In HNLC regions, a buffering capacity of H_2S is much larger than that of non-HNLC regions due to the additional supply of sulfur compounds from volcanic gas (H_2S , SO_2 , H_2SO_4) and volcanic ash (S, metallic sulfates), leading to the more abundant product of H_2S not only from the volcanic gas but also from the enhanced sulfate reducing bacteria (SRB). Therefore, both iron and sulfide may be hard to penetrate into the overlying surface ocean but rather be pulled down into the hypoxic deep sediment (~1,100m) with abundant Fe (~565 μM) and H_2S (~150 μM), as observed by Aguilina et al.(2014) in the deep ocean of the Southern Ocean, the largest HNLC region. Fig. 3 shows the pathways of iron and sulfur prior to algae assimilation in both of non-HNLC (broken line) and HNLC (solid line) regions, which vividly implies the enhanced production of H_2S with sulfur compounds from volcanic eruptions in HNLC regions to be markedly more changed from $\text{Fe}^{2+}(\text{aq})$ to FeS and FeS_2 transformations.

[14] Simultaneous locking of Fe and S in the form of insoluble black FeS ($4.4 \times 10^{-5} \text{ g/100g H}_2\text{O}$) and pyrite (FeS_2), can be thus enhanced by the abundant supply of sulfur compounds during or after the volcanic eruptions in the HNLC regions. In other words, volcanic sulfur pulls down iron toward FeS/FeS_2 sedimentation and thus there is no key to unlock the sedimentary pyrite (FeS_2) formation except the iron-and sulfur-oxidizing bacteria such as *Acidithiobacillus ferrooxidans*, *Alicyclobacillus* and *Sulfobacillus*, living in pyrite deposits to metabolize ferrous iron and sulfur and producing sulfuric acid, with optimal pH (1.3~4.5), far acidic than that of ocean (7.8~8.4). Such an exceptional pyrite oxidation has been observed at the marine shore sulfidic mine in northern Chile with extreme acidity (1~4) and high salinity (10~20 cm thick salts) (Korehi et al., 2013). Therefore, HNLC regions have a stronger lock of sulfur compounds without key of iron sulfides than that of non-HNLC regions, which leads to the present iron limited and resultantly "low chlorophyll (LC)" waters, while nitrate, phosphate and silicate incorporated into the organic material through photosynthesis

are released to the ocean during bacterial respiration to be accumulated as "high nutrient (HN)" in the HNLC regions. Block diagram leading to HNLC regions is schematically simplified in Fig. 4.

- [15] As shown in Fig. 5, algae utilize the dissolved iron, $\text{Fe}^{2+}(\text{aq})$ with competition of insoluble FeS/FeS_2 , the latter being significant if the volcanic activity is stronger for the sulfur contribution than the desert contribution for iron. Soluble Fe sulfates in Fig. 5 are FeSO_4 , $(\text{Fe})_2(\text{SO}_4)_3$, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ and insoluble Fe sulfides are FeS and FeS_2 , while soluble non-Fe sulfates are $\text{Al}_2(\text{SO}_4)_3$, NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{SO}_3$, BeSO_4 , CdSO_4 , CuSO_4 , MgSO_4 , MnSO_4 , NiSO_4 , KHSO_4 , Pb_2SO_4 , Na_2SO_4 and $\text{Na}_2\text{S}_2\text{O}_3$. Insoluble non-Fe sulfates are Ag_2SO_4 , BaSO_4 , PbSO_4 , Hg_2SO_4 , RdSO_4 and SrSO_4 , while soluble sulfide is H_2S and insoluble sulfides are CdS , CuS , PbS and PoS . As seen in Fig. 5, H_2S is produced by 4 routes; 1) directly from volcanic gas with relatively high solubility ($0.3\text{g}/100\text{g H}_2\text{O}$) compared to that of FeS (4.4×10^{-5})
- [16] 2) from sulfur by sulfur oxidizing bacteria such as *Beggiatoa*, 3) from soluble sulfate by sulfate reducing bacteria such as *Desulfovibrio desulfuricans*, 4) from soluble sulfides by hydrogenation. The more H_2S available from either the volcanic gas and sulfur oxidation, or soluble sulfates through sulfate reducing bacteria and soluble sulfides, the more sedimentation occurs in the forms of FeS and FeS_2 . Therefore, it can be seen that the volcanic eruption enhances the formation of FeS and FeS_2 , which allows less and less Fe available to algae to be iron limited condition of "LC" (low-chlorophyll). On the other hand, nutrients such as nitrate, phosphate and silicate are fairly soluble to be utilized by algae. However, if Fe is limited, the growth of algae is retarded and thus nutrients are less utilized and further enriched to be "HN" (high-nutrient).
- [17] Oceans with iron limitation can be thus categorized by 4 regions depending upon the relative rates of accumulation for iron and sulfur, $(dS-dFe)/dt$ in the large order of LNLC, HNLC, LNHC and HNHC, as summarized in Table 2 and 3. In order to confirm the present concept of 4 different regions depending upon the iron and the sulfur, an aerated batch experiment was carried out at 250ml flask with 150ml medium under $100 \mu\text{mol}$ light intensity for *Chlorella vulgaris*. JM medium (Thompson et al., 1988) without Fe was used as the base medium and coded as (-Fe) or HNLC, whereas JM medium itself was coded as (+Fe) or HNHC. Fresh volcanic ash was collected from Mt. Ontake of Japan, erupted on the 27th of September, 2014, with the composition of Fe; 33312.0 and S; 29531.4mg/kg as determined by ICP (Optima 5300DV, Perkin Elmer). Clay was collected from Tongyoung City of South Korea with the composition of Fe; 26013.5, S; 1350.4mg/kg. 100% of the volcanic ash (0.1g) without clay was added to the 150ml JM medium without Fe, whose result was shown in Fig. 6 with code of (V100) or LNLC. 75% of the clay mixture with clay 0.075g and volcanic ash

0.025g was added to the 150ml JM medium without Fe, whose result was seen in Fig. 6 with code of (C75) or LNHC.

[18] Table 2

[Table 2]

Regions		Accumulation Rate			Relative Magnitude
		Iron(dFe/dt)	Sulfur(dS/dt)	($dS-dFe$)/ dt)	
LC	HNLC	+	++	+	$0 > dFe/dt < dS/dt$ $\gg 0$
	LNLC	-	++	++	$0 > dFe/dt \ll dS/dt$ $\gg 0$
HC	HNHC	++	-	--	$0 \ll dFe/dt \gg dS/dt$ < 0
	LNHC	++	+	-	$0 \ll dFe/dt > dS/dt$ > 0

[19] Table 2. Accumulation rates of iron and sulfur compounds for 4 cases of regions. (- ; descending, -- ; significantly descending, + ; ascending, ++ ; significantly ascending)

[20]

[21] It is thus expected that LNLC regions can be temporally changed to LNHC regions although not for a long time due to the limited amount of the Fe-replete composite for the large-scale iron fertilization. It is thus postulated that the future iron enrichment experiment can be carried out either in HNLC, as done so far during the last 20 years, or in LNLC regions, most preferably in the boundary of Mariana Islands, Hawaii, Guam of the U.S. Territory and Iceland, as long as some sort of the external iron supply is followed in large scale along with minor techniques allowing the Fe-replete composite to stay within 100m deep surface for diatoms assimilation of iron.

[22] Note that iron is available mainly from 3 sources of desert, volcano and upwelling while sulfur is available from 2 sources of volcano and desert, the latter being negligible due to its sulfur wash-out for long time by rainfall and weathering. Note also that the Antarctic is not only the HNLC regions of the Southern Ocean but also one of 8 major great fishing areas of LNHC. This duality can be caused by the copresence of Continental deserts and volcanos. The carriers of the inorganic nutrient pool in Fig. 7 are Winds and Currents, which have seasonal variations. Therefore, 4 cases of HNLC, LNLC, HNHC, and LNHC can have their own variations with seasons. Sulfate-reducing bacteria(SRB) are widely distributed in deep water and sediments of lakes, rivers, and oceans. With the capacity to use sulfate, thiosulfate or even elemental sulfur

as electron receptors instead of oxygen in their respiratory chain, they participated in the recycle of elemental sulfur in nature. SRB produces H_2S from soluble FeSO_4 or $\text{Fe}_2(\text{SO}_4)_3$, which is ultimately transformed to insoluble FeS and FeS_2 . Therefore, H_2S depletes Fe and lead to the Fe limited zone. In non-HNLC regions, not many sulfur compounds are present except those from algal or animal decomposition. In HNLC regions, however, many sulfur compound are supplied from volcanoes. Thus, there were abundant H_2S pool as observed in the Sourthern Ocean. On the contrary, there can be not many H_2S in non-HNLC due to lack of external supply of sulfur compounds. Abundant SRB in the deep ocean (~1,100m) of HNLC regions(Aguilina, 2014) might be the sign of the facilitated sedimentation of Fe starved zone in HNLC. There can be a continuous sedimentation of $\text{Fe}^{2+}_{(\text{aq})}$ in forms of FeS and FeS_2 by H_2S pool, produced by SRB under hypoxic conditions such as in swamps or dead zones of lakes and oceans. Therefore, most of Fe supplied to the HNLC regions, internally by algal and bacterial decompositions or externally by aeolian dust and volcanic ash, will be eventually converted to insoluble FeS and FeS_2 in the hypoxic deep ocean of HNLC regions unless assimilated to phytoplankton within the surface distance of about 100m or so. In HNLC regions, Fe will be supplied by either wind-driven upwelling(as is at the Gulf of Alaska in the Subarctic Pacific and at the Galapagos Islands in the Equatorial Pacific) or temperature-driven hydrothermal vent(as is in the Southern Ocean). Regardless of HNLC or non-HNLC regions, additional driving force of Fe flux(amount per unit area per unit time) will be available from the concentration gradient of dissolved oxygen between the hypoxic deep ocean with plenty of decomposed Fe as source of Fe and the oxic surface ocean with Fe-starved algae as sink of Fe. In HNLC, however, the amount of Fe available to algae was far less(0.000004 ppm) than that in non-HNLC regions(0.0034 ppm) due to much more sedimentations of FeS and FeS_2 by relatively abundant supply of sulfur from the volcanic eruptions in HNLC compared to the input of iron from the desert dust. In Table 4, flux and gradient with source and sink in HNLC regions were summarized, which implied that there could be simutaneously momentum, heat and mass fluxes in HNLC regions. The hypoxic condition in the deep ocean allowed the sulfate-reducing bacteria(SRB) (*Desulfovibrio*~40 μm), surviving only one day in air, to produce H_2S and Fe^{2+} , the latter being partly engulfed by bacteria for their own concentrated growth($10^8\sim 10^9$ cells $\cdot\text{mL}^{-1}$). SRB produced H_2S and metal ions along with Fe^{2+} from high sulfates in the hypoxic water, while HNLC regions with extensive volcanic eruptions were enriched with sulfur compounds of S, H_2S , SO_2 , H_2SO_4 and sulfates with FeSO_4 to produce more H_2S and Fe^{2+} , which might lock and hold more Fe^{2+} in forms of FeS and FeS_2 to be less Fe^{2+} available to algae in the surface ocean. Besides, the bacterial growth in the hypoxic water was further enhanced by the abundant supply of Fe^{2+} from iron sulfate through

their own sulfate-reducing activity. As the more sulfate is available from volcanic eruptions, the more H_2S is produced in HNLC regions, which leads to locking more Fe^{2+} to the sediment in FeS and FeS_2 precipitates. Therefore, HNLC regions are Fe-limited due to the relatively abundant supply of sulfur compounds from the extensive volcanic eruptions. Especially, the Southern Ocean with fast (~4km per hour) and the largest volumetric flow rate ($1.47 \times 10^8 \text{ m}^3$ per second at Tasmania) of the Antarctic Circumpolar Current and yearly continuous volcanic eruptions at Mt. Erebus allow a lot of sulfur compounds with fast dissipation into its deep ocean, associated with leaving the highest nutrients (N, P, Si) among global HNLC regions to be "high nutrients" while Fe is mainly sedimented in FeS and FeS_2 by enriched pools of H_2S and SRB to be Fe-limited or "low chlorophyll".

[23] Table 3

[Table 3]

Flux	Momentum	Heat	Mass					
Gradient	Current flow rate (v)	Temperature (T)	Dissolved Oxygen (DO)	$\text{Fe}^{2+}_{(\text{aq})}$	FeS	H_2S	Algae	Sulfate Reducing Bacteria (SRB)
Surface Ocean	+	+	+	-	-	-	+	1)-
Deep Ocean	-	-	-	+	+	+	3)-	2)+

[24] Note; 1) SRB survives only one day under air exposure.

[25] 2) $10^8 \sim 10^9 \text{ cells} \cdot \text{mL}^{-1}$

[26] 3) dead or sinking algae

[27] Table 4. Source(+) and sink(-) of fluxes in the surface and deep oceans of HNLC regions.

[28]

Solution to Problem

[29] The present invention may enable us to decide the appropriate location for the large-scale iron enrichment experiment to reduce the atmospheric CO_2 with several criteria as below.

[30] As the future candidate of optimal locations, Hook Ridge in the Central Basin of the Bransfield Strait of the Southern Ocean and Shag Rocks (200×50km) of South Georgia in northern Scotia Sea are suggested by the following reasons.

- [31] 1) Volcanic aspects to avoid the sulfur compounds.
- [32] - Not over the boundaries of the Earth plate (for Hook Ridge), but just outside of northern Scotia plate (for Shag Rocks)
- [33] - Far from active volcanoes and earth quakes (for Shag Rocks)
- [34] - Low concentrations of sulfur compounds (S^0 , SO_3^{2-} , SO_4^{2-} , H_2S , SO_2) to minimize iron sulfide formation,
- [35] 2) Iron input as many as possible for algal blooms.
- [36] - Downwind region of the Patagonian and Chile deserts for aeolian supply of minerals with iron (for Shag Rocks)
- [37] - Near to rocky islands covered partly with ice for self aeolian dust flux input and nutrient enriched ice melt (for Shag Rocks)
- [38] - Wind-driven upwelling, density-driven vortex mixing, and previous volcanic eruption with abundant iron sediments due to submarine volcanic eruption as a pool of dissolved iron in the pore deep ocean (for Hook Ridge)
- [39] - Not bulk scale additions of direct iron or iron sulfate, but deploying natural clays or soils available nearby islands with possible content of iron in the range of 3.5 to 6wt%, as observed elsewhere in the Continents, along with volcanic ash desulfurized by rainfall and weathering for long time,
- [40] 3) High momentum flux for fast dispersion around the experimental zone.
- [41] - Cold and fast Weddell Sea Deep Water passes through to meet the warm waters of the Subarctic, creating a zone of upwelling nutrients (for Shag Rocks)
- [42] - Located in-between the South America and the Antarctic with narrowest Drake Passage providing the Antarctic Circumpolar Current with high linear flow velocity ($\sim 4\text{km per hour}$, v) and the largest ocean current ($1.25 \times 10^5 \text{ m}^3$ per second) for fast deployment of the Fe-replete complex(mA) over wide oceanic surface area with high momentum flux($\text{mA} \cdot v$) in large scale iron fertilization,
- [43] 4) Nutrients for effective algal bloom to be near "high chlorophyll(HC)"
- [44] - Region where cyanobacterium *Synechococcus* live as initial efficient grazer of iron
- [45] - Abundant coccolithophorids and silicoflagellates are dominated in Weddell Sea, which passes through (for Shag Rocks)
- [46] - High concentration of silica or silicic acid for proper growth of diatoms such as *Corethron criophilum*, *Chaetoceros neglectus*, *Chaetoceros dictyota* (de Baar et al., 1990), which are invulnerable to predation by zooplankton and sink rapidly (0.96 m d^{-1}) upon death for efficient sequestration of atmospheric CO_2
- [47] - A place where the Antarctic krill and humpback whale are currently present with stable food webs ecosystem,
- [48] 5) Environmental aspects to increase the probability of successful iron enrichment experiment

- [49] - Not far from sources of search and rescue
- [50] - Experimental period can be the duration between November and April or preferably January for high irradiance and warm water temperature with high ice melt for phytoplankton bloom.
- [51]
- [52] There can be a few possible low chlorophyll(LC) of LNLC regions around the world in addition to the current well-known HNLC regions. Iceland, Mariana Islands-Guam, North Pacific Subtropical Gyre and Hawaii are suggested as LC regions due to abundant sulfur compounds available from either submarine or subaerial volcanic eruptions to pull down the iron in forms of FeS and FeS₂ to the ocean sediment and furthermore its oceanic dispersion flow pattern is blocked or surrounded by Winds and Currents to be isolated from neighboring oceans. Such LNLC regions can be temporarily turned to LNHC regions so long as continuous supply of iron in large scale is provided, which may allow not only the sequestration of atmospheric CO₂ but also the great fishery. Iceland is located in-between Arctic Ocean and North Atlantic Ocean of Mid-Atlantic Ridge with division between European and North American tectonic plates. The island has 130 active volcanoes with downward cold Currents (East Greenland and East Icelandic) and upward warm Currents (North Atlantic and Icelandic) along with Winds (Easterly/Westerly/Icelandic Low/North Atlantic Oscillation) and even dust storms from Southern Iceland. Bioassay experiment by Nielsdottir(2009) showed nitrate(2.83~5.00μM), silicic acid(0.03~0.70μM) and chlorophyll(0.24~0.58μgℓ⁻¹), which is close to those of the Subarctic Pacific in Table 1. As for the Mariana Islands, Japan has 108 active and extinct volcanoes in brackets with two tracks, one is Hokkaido(17), Honshu(46), Izu Islands(12), others(12) and another is Kyushu(10) and Nansei Islands(11). The tectonic plates surrounding Japan are Pacific, Philippine Sea and Okinawa plates. The volcanoes from Ryukyu Arc and the Izu-Bonin-Mariana Arc embrace together partly western Pacific Ocean and Philippine Sea up to Mariana Islands. Japan has downward cold Current of Oyashio from Kamchatka and upward transverse warm Currents of Kuroshio and North Equatorial while strong typhoon pushes upwards during the summer. Therefore, there can be a convergence zone in front of Osaka surrounded clockwise by Zamami Island (famous for humpback whale watching), Nanpo Islands, Mariana Islands, Okinawa Islands and Kyushu volcanoes. Lin et al. (2011) showed the fertilization potential near the Anatahan volcano (146°E, 16°N) in the Northern Mariana Islands of western North Pacific Subtropical Gyre with the concentrations of nitrate (0.042μM), phosphate (0.003μM) and iron (0.002μM) to claim the most oligotrophic LNLC ocean deserts on Earth. Due to the political conflicts in the Northern Mariana Islands and its too close to the Anatahan volcano, the future fertilization experiment can be considered at

somewhere near to U. S Territory of Guam.

- [53] Hawaiian volcanoes are located in the middle of the Pacific plate while Hawaiian Hotspot between the Hawaiian Ridge and Emperor Seamount chain is composed of more than 80 large volcanoes, which shows the step-wise development of volcanic activity such as submarine preshield stage (Loihi Seamount), shield stage with caldera while submerged, explosive subphase with volcanic ash, subaerial subphase (currently active Hawaiian volcanoes) and finally postshield stage (atoll and eventually seamount). Hawaiian archipelago has 15 active volcanoes with opposite directional currents (westerly North Equatorial and easterly Equatorial Countercurrent) in the North Pacific Gyre and NE Trade Wind. The extent of LNLC characteristics can be significant in Iceland since Iceland has much more active volcanoes (130) even excluding neighboring Greenland (500) than those of Japan (108) and Hawaii (15) and more surrounded by Currents and Winds to be partly isolated from the Arctic Ocean and the North Atlantic Ocean.
- [54] Since the dissolved iron is engulfed by picoplankton to be grazed by diatoms and subsequently by copepods, krill, and finally by small fish or by whale. Humpback whale with worldwide population of about 10,000~15,000 feeds krill, copepods and small fish. Humpback whale has been observed not only in 3 HNLC regions of the Subarctic Pacific (Alaska), the Equatorial Pacific (Galapagos) and the Southern Ocean (Drake Passage, South Georgia), Antarctic Peninsula (south of Cape Horn) but also in other 4 locations of Iceland (Snaefellsnes peninsula), Japan(Zamami), Guam, and Hawaii(Maui). It can be thus postulated that humpback whale is a good biomarker for the location of the future iron enrichment experiment. In other words, such an iron experiment may be better to be carried out somewhere humpback whales feed and breed since the fertilized iron can be fed by the phytoplankton to be grazed by copepod and krill, and eventually by humpback whale. July is usually the mating season for Southern Hemisphere humpback whales, with births occurring in June of the subsequent year. A calf is generally strong enough to migrate with its mother at three months old. Since humpback whale feeds krill and small fish at the Antarctic during the winter while it breeds at the tropical or subtropical oceans during the summer, it is suggested to start the iron fertilization experiment during the early summer of January with warm coastal temperature(-3~15°C) and sufficient irradiance. At the time when humpback returns to the Southern Ocean after long journey from the Northern Hemisphere tropical or subtropical oceans, the iron stimulated area in someplace of the Southern Ocean may have already algal bloomed with friendly eco-system community of heterotrophic bacteria, picoeukaryotes and picoplankton, diatoms, copepods and krill if the intended iron enrichment experiment in large scale is successful.

Advantageous Effects of Invention

- [55] There can be 4 special cases depending upon both of nutrients (high and low) and chlorophyll (high and low); HNLC(high-nutrient-low-chlorophyll), HNHC (high-nutrient-high-chlorophyll), LNLC(low-nutrient-low-chlorophyll) and LNHC(low-nutrient-high-chlorophyll).
- [56] The case of HNLC can be possible if the accumulation rate of sulfur from volcano (dS/dt), is far greater than the accumulation rate of iron from desert, (dFe/dt) to be $0 > dFe/dt < dS/dt \gg 0$. Since iron is essential to algal growth, it can be “HC” if (Fe-replete) while “LC” if (Fe-starved). If iron reacts with volcanic sulfur to be precipitated in FeS and FeS_2 , 4 cases can be classified as shown in Table 2 depending upon both of relative accumulation rates of iron and sulfur.
- [57] As for the case of LNHC when $0 << dFe/dt > dS/dt > 0$, there are 8 great and important fishing areas with cross flow of cold and warm waters. As seen in Table 3, LNHC regions have broad supply of aeolian dusts from deserts along with ample volcanoes, which may allow the algal growth to induce great to induce great fishing areas. Note that the Southern Ocean is the largest HNLC regions while the Antarctic is also one of 8 world fishing hot spots of LNHC (Table 3) at the same time, whose duality can be caused by its largest area of the Oceans with one part of HNLC and another part of LNHC. It's probably worth noting that since the Earth is 70% water, undersea volcanic eruptions are common, as seen massively in Greenland. Observed effects on the surface are rare except for really shallow ones. Therefore, there can be massive underwater volcanic eruptions in HNLC regions than commonly observed, leading further to the criteria of HNLC regions if volcanic mountains are well distributed around such regions, as seen in the Subarctic Pacific enclosed by Aleutian Arc/Augustin volcanoes, in the western North Pacific Gyre, Ryuku Arc and Izu-Bonin-Mariana Arc, East Equatorial Pacific near Galapagos Islands, 26 Peru and Chile volcanic mountains, western Iceland with 130 volcanic mountains, the latter reshaping Arctic Ocean floor.
- [58] Table 4

[Table 4]

Regions		Typical Regions	Nutrient Sources	
			Desert	Volcano
LC	HNL C	1. Southern Ocean 2. Equatorial Pacific 3. Subarctic Pacific	1. Australian/ Patagonian/ South Africa 2. Gobi/Chile 3. Gobi	1. Erebus(Antarctica)/ Huaynaputina(Peru)/Hudson (Chile) 2. Huaynaputina(Peru)/Hudson(Chile)/ Galapagos Islands 3. Aleutian(USA)/Augustine (USA)/Kasatochi(USA)/Redoubt(USA)
	LNL C	1. Mariana Islands 2. Hawaii 3. North Pacific Sub-tropical 4. Iceland	1. Gobi 2. - 3. - 4. Arctic, Southern Iceland	1. 108 Active and extinct (Ryuku Arc and Izu-Bonin Arc) 2. 15 Volcanoes 3. 80 Volcanoes (Hawaiian Ridge Emperor Seamount Chain) 4. 130 Active Volcanoes

HC HC	HNH C	Benguela upwelling system (15° S - 35° S)(Southwestern Africa)	Kalahari, Namib	None active but extinct ; Angola (0), Namibia (1). South Africa (4)
	LNH C	1. Pacific coast of Mexico2. Northeast Pacific (Alaska)3. Northwest Pacific4. Northeastern coast of Canada5. Peruvian Coast6. Pacific coast of New Zealand7. Southern and southwestern coast of Africa8. The Antarctic	1. Chihuahuan, Sonoran, Mojave2. Gobi, Great Basin3. Gobi4. Arctic, Sahara5. Patagonian, Atacama6. Great Victoria, Great Sandy, Gibson, Simpson7. Kalahari, Namib8. Antarctic, Great Victoria, Great Sandy, Gibson, Simpson, Patagonian, Atacama, Kalahari, Namib	1. Barcena, Socorro, and 9 others2. Augustine (8), Kasatochi, Redoubt (5)3. Hokkaido(17), Honshu(46), Pavolf (40), Cleveland (19)4. Greenland, Iceland, Newfoundland. Seamounts, Fogo Seamounts5. Ubinas, Sabancaya and 24 others in Peru and Chile6. White Island, Kermadec Islands7. Madagascar (5), Mozambique(1),Tanzania(22),South Africa (4)8. Erebus and 11 Holocene

[59] Table. 4. Corresponding typical regions and nutrient sources.

[60] In order to examine the present hypothesis for HNLC criteria in terms of both of the relative accumulation rates of iron and sulfur as $0 > dFe/dt < dS/dt \gg 0$, the southern Omani coast was chosen since the previous study by NASA research team proposed the Omani coast of the Arabian Sea as HNLC during the late Southwest Monsoon (Naqvi et al., 2010). The Omani coast is located on the tectonic boundary of the Oman plate with S-replete extensive mud volcanoes at Borborok, Napag and Pirlgel with seven active craters, while major deserts such as Arabian and Syrian are mobilizing their Fe-replete dust across 150 km long desert area to be mostly blocked by high

Omani mountains (~3,000m) and Southwest Monsoon so that most of desert dusts except Iranian and Thar can not reach on the surface of the Omani coast. Nearby the southern Omani coast, there are many active and extinct volcanoes in the bracket at Yemen(13), Saudi Arabia(24), Iran(7), Iraq(1), India(4) and Pakistan(7). Therefore, the contribution of sulfur from the volcanoes to the southern Omani coast can be far greater than that of iron from the deserts, which may be the reason why the southern Omani coast was regarded as HNLC by the NASA research team.

- [61] Interestingly enough, Indonesia has 127 active volcanoes but no desert. However, western Australian dust originated from deserts of Great Victoria, Great Sandy, Gibson, Tanami and Little Sandy dump the iron enriched dust to Indonesia. Besides, Java Sea is surrounded by active volcanoes while the eastward South Java Current flows along the coast during the Northwest Monsoons. The westward South Equatorial Current flows away from the coast along the Sunda Islands, south of the Lombok Strait of Java with chlorophyll-a of $0.2 \sim 1.0 \mu\text{g}\ell^{-1}$ while nutrients such as nitrate ($0.5 \sim 1.5 \mu\text{M}$), phosphate ($0.05 \sim 0.4 \mu\text{M}$), silicate ($4 \sim 14 \mu\text{M}$) and chlorophyll-a ($0.3 \sim 1.0 \mu\text{g}\ell^{-1}$) were monitored in the northern coastal area of Java Sea, where is a major fishing ground in Indonesia contributing 31% of the national marine fisheries production. Since 2006, fishers have observed humpback whales off Bontang, northeast of the Mahakam Delta in East Kalimantan. It can be thus suggested that Java Sea of Indonesia is another LNHC region in the world. Therefore, the present scheme of differentiating HNLC, LNLC, HNHC and LNHC in terms of the relative magnitude of the accumulation rates of iron and sulfur appears to be plausible.

- [62] As reviewed by Shaked and Lis in 2012, small phytoplankton are favored under Fe limitation. On the basis of relative scale of Fe availability established from phytoplankton uptake rates, picoplankton such as *Synechococcus* and *Synechocystis* appear to be grazed by diatoms such as *Thalassiosira* spp. and *Chaetoceros* spp., flagellates of *Phaeocysts* spp. and dinoflagellates of *Chrysochromulina* *ericina*. Such results are in good agreement with other results for four size classes ($0.2\sim 2$, $2\sim 5$, $5\sim 20$, and $>20 \mu\text{m}$) of Fe cycle with the highest Fe uptake rate of picoplankton. It was suggested that copepod numbers can be controlled by a combination of competition and predation by krill, the latter being fed by humpback whale. It can be thus postulated that the route of Fe availability starts from picoplankton, diatoms, copepods and krill to the final destination of humpback whale. Therefore, in order to make a successful algal blooms for feasible atmospheric CO₂ sequestration, the size of Fe source must be smaller than that of picoplankton ($<2 \mu\text{m}$). Since Fe in the aeolian dust was in the size of $0.3\sim 1 \mu\text{m}$ and summer krill were mainly in the top 100m layer(Sverdrup, 1953) where cyanobacterium picoplankton stay for efficient photosynthesis and N₂-fixation, it is important to deploy the Fe enriched eco-friendly composite on ocean surfaces in

components of Fe-replete fine silt and clay (11% compared to 3.5~6% of the aeolian dust), water-buoyant floating enhancer such as carbon black ($\sim 0.1\mu\text{m}$), biodegradable plastic foamed poly lactic acid and fine wood chip from sawmill ($< \sim 1,400\mu\text{m}$) and iron-reducing marine bacterium *Shewanella* algae to reduce ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}) for facilitated assimilation to picoplankton. Since the wood chip is far greater than other components and its density is less than that of water, the wood chip may play a role of floating moiety whose surface is covered with iron oxides ($0.05 \sim 0.1\mu\text{m}$) from clay particles and reinforced carbon black ($\sim 0.1\mu\text{m}$) and *Chewanella* algae ($\sim 1.5 \times 10^7$ CFU, colony-forming unit) with 100% survival in cold seawater (2°C) over a period of 1 to 2 months (Gram et al., 1999). It is important to design appropriately the Fe enriched eco-friendly composite to be stayed longer on the top water ($< 100\text{m}$) to be readily available to algae rather than to be sedimented downwards and reacted with sulfate enriched ions to be insoluble FeS , which leads to the retardation of algal growth due to lack of iron.

- [63] The extracellular carbohydrate polymers from five desert soil algae with different cohesion were studied (Hu et al., 2003) in the stabilization of fine sand grain in the sequence of the great kinematic viscosity of *Desmococcus olivaceus* (1.1474), *Scytonema javanicum* (1.0278), *Nostoc* sp. (1.0149), *Phormidium tenue* (0.967), and *Microcoleus vaginatus* (0.9434), which all belong to cyanobacteria except *Desmococcus olivaceus*. Among them, *Scytonema javanicum* and *Nostoc* sp. are N_2 - fixing marine cyanobacteria. To minimize the occurrence of FeS in the ocean, the best strategy of Fe-replete eco-friendly composite is to be floated on the surface of ocean as long as possible until its finely pulverized Fe component is assimilated to algae for their growth. Therefore, such two N_2 -fixing desert soil algae can be used not only as the Fe-replete eco-friendly binder but also as a buoyancy promoter due to their copious viscous mucilage. Besides, agar from agaphyte may spherically encapsulate such a Fe-replete composite for better floating to be efficiently grazed by phytoplankton in the seawater.
- [64] Special precaution may be followed in the preparation of Fe enriched composite, not to violate the United Nations Convention on Biological Diversity (CBD) and the London Convention on the dumping of wastes at sea, as happened near the islands of Haida Gwaii in 2012. For the future iron fertilization, the deployment of Fe replete composite can be not in the common mode of FeSO_4 bubbled with SF_6 tracer, but in the mode of eco-friendly composite over the surface water of the fast flow rate ($\sim 4\text{km}$ per hour) of the Antarctic Circumpolar Current (ACC) and locate a few fertilizing ships at the same time to be perpendicular to ACC streamline for wide even distribution on the surface water not in patch length scale but in large scale ($\gg 10\text{km}$) as suggested by Boyd et al., (2007).

- [65] In the present study, 6 new candidates for the successful location of the future iron fertilization are proposed as; 1) Bransfield Strait in Drake Passage of the Southern Ocean, 2) Shag Rocks of South Georgia in Scotia Sea of the Southern Ocean, 3) Mariana Islands-Guam, 4) Hawaiian Islands, 5) North Pacific Subtropical Gyre, and 6) west Iceland, all of which the humpback whales currently feed and breed. The most preferable location can be Shag Rocks (42° W)(200×50km) of South Georgia due to the following reasons; 1) located at outside of major tectonic plate and micro plate boundaries (Barker, 2001), 2) located where the high nutrient (22.2 ~ 28.8 μM nitrate) and high chlorophyll (0.46 ~ 0.93 $\mu\text{g}\cdot\ell^{-1}$) were present (Koike, 1986) while Antarctic Circumpolar Current dominated by diatoms cross flows with the Weddell Sea Deep Water dominated by coccolithophorids and silicoflagellates, 3) located at the South of the Polar Front dominated by diatoms, 4) located not far (185km) from South Georgia Island (170×40km) which is the unique position inside the Antarctic Convergence yet outside the limit of the yearly sea ice to be home to tens of millions of breeding penguins, 300,000 elephant seals, 3 million fur seals, and 25 species of breeding birds, implying its good location for phytoplankton productivity, 5) located not far from the forgotten whale station of Grytviken in South Georgia, which has been open in 1904 but closed in 1966 due to lack of whales. Since there are still massive elephant seals, fur seals, and king penguins at Grytviken but no humpback whales around, the latter feeding krill, plankton, and small fish, Grytviken can be a good base camp for the iron fertilizing ships and their crew residence not for several weeks, as commonly done in the previous 14 mesoscale iron experiments, but for several months or even years to apparently observe the iron stimulated productivity by satellite for chlorophyll and DMS. On-line monitorings of the algal removal rates of nitrate, phosphate and silicate by corresponding sensors, the algal production rates of dissolved oxygen (DO) in ocean and oxygen in atmosphere by DO and O_2 sensors, the algal consumption rates of dissolved carbon dioxide (DCO_2) in ocean or the fugacity of CO_2 in atmosphere by CO_2 sensors and the production rate of chlorophyll by chlorophyll sensor system can be continuously proceeded at fertilizing ships to see the effect of the iron fertilization. The light-dependent reaction of photosynthesis requires inorganic phosphate to convert H_2O to O_2 , which leads to the increase of dissolved oxygen (DO) and thus the uptake rate of the phosphate and iron are also increased during the daytime for ATP production. Therefore, the iron deployment will be made during the daytime. The rate determining step for nitrogen uptake at the Fe-replete condition is the step from the nitrate (NO_3^-) to the nitrite (NO_2^-) with electron transfer of NADPH under nitrate reductase, while the one at the Fe-starved condition is the step from the nitrite (NO_2^-) to the ammonium (NH_4^+) with electron transfer of ferredoxin (Walsh and Steidinger, 2001). Since the nitrate reductase prefers the anaerobic condition, the nitrogen uptake

is mainly occurred during the nighttime, which is in good agreement with the diel variation of *Synechococcus* spp. of maximal cell concentration at midnight (Tsai et al., 2012). It is thus expected that *Synechococcus* grows during the night. However, diatoms are capable of dividing at any point of the diel cycle (Yool and Tyrrell, 2003). Therefore, the monitorings of chlorophyll, nitrate phosphate, and silicate concentrations after deploying the Fe-replete complex can be made throughout the day and the night for the accurate estimation and prediction of algal blooms.

- [66] The symptom of such a successful iron fertilization experiment can be seen by the increased rates of chlorophyll, DMS, DO, O₂, pCO₂, fugacity of atmospheric CO₂, concentrations along with the decreased rates of nitrate, phosphate, silicate concentrations while dominant plankton moves in the sequence of picoplankton, diatoms, copepods and krill to observe the return of humpback whale, for example, to Grytviken. Besides, such an iron fertilization should be carried out not in common mesoscale patch but in large scale for commercial feasibility of sequestering atmospheric CO₂ to be attractive not only to scientific groups but also big international companies for realistic commercialization of atmospheric CO₂ sequestration in compliance with Kyoto Protocol, under which emissions from developing countries are allowed to grow in accordance with their development needs, and countries actual greenhouse gas emissions have to be monitored and precise records have to be kept of the trades carried out. Humpback whales over 10,000 ~ 15,000 worldwide live at the surface of the ocean, both in the open ocean and shallow coastline water. When not migrating, they prefer shallow waters. They migrate from warm tropical waters where they breed and calve to Arctic waters where they feed krill, plankton and small fish. In order to be successful in iron fertilization, its precise location can be shallow coastline water with abundant krill and copepods, the latter feeding ciliates and heterotrophic flagellates eating phytoplankton. Since HNLC regions are rich in nitrate, phosphate and silicate but starved iron, the iron fertilization is expected to increase the phytoplankton productivity starting from picoplankton until copepods and krill are abundant, which may induce in the long run the possible biomarker of the humpback whale to return to the vicinity of the forgotten whale station of Grytviken in South Georgia to convince the success of the iron fertilization, which can be cross-checked by satellite images of nitrate, chlorophyll and DMS(dimethyl sulfide) along with on-line database established by chlorophyll sensor to see the time and the extent of the transition from the current status of HNLC region before iron fertilization to the new status of LNHC region after iron fertilization, the latter being observed at 8 major fishing hot spots.

- [67] The optimal location for the large-scale sequestration of atmospheric CO₂ can be achieved if the iron fertilization is carried out not only as close to deserts but also as far from volcanoes, earthquakes and boundaries of tectonic plates. Fe-replete compounds

are designed to stay as long as possible within 100m surface ocean with aid of complex consisting of natural aeolian dust and/or clay, volcanic ash, mucilaginous cyanobacteria. Such a Fe-replete complex is encapsulated by agar so that phytoplankton can digest easily and slowly prior to its sinking to the deep ocean where iron is changed to iron sulfide(FeS) and eventually pyrites(FeS₂).

[68] Oceans are firstly categorized by 4 groups such as 2 LC (HNLC, LNLC) and 2 HC (HNHC, LNHC) regions on the basis of the relative degree of the accumulation rates for iron from deserts and for sulfur from volcanoes.

[69] It is suggested to deploy the large-scale iron fertilization in terms of the high linear flow velocity(~4km/h) at the Antarctic Circumpolar Current in order to have a high momentum flux for the well dispersion of the Fe-replete complex.

[70] Humpback whale is proposed as a biomarker for the successful iron fertilization in large-scale since humpback whale feeds krill, which feed cockpods and diatoms. The fast sinking rate of diatom(0.96 m d⁻¹) is very attractive for sequestration of CO₂.

Brief Description of Drawings

[71] Figure 1 is a diagram illustrating that Fe may be released from the sediments as more available reduced Fe²⁺ prior to algal blooms.

[72] Figure 2 is a diagram illustrating that iron ion in either seawater or freshwater can be minimally satisfied to synthesize chlorophyll-a containing algae cell.

[73] Figure 3 is a diagram illustrating that the pathways of iron and sulfur prior to algae assimilation in both of non-HNLC (broken line) and HNLC (solid line) regions.

[74] Figure 4 is a block diagram leading to HNLC regions.

[75] Figure 5 is a diagram illustrating that algae utilize the dissolved iron, Fe²⁺_(aq) with competition of insoluble FeS/FeS₂, the latter being significant if the volcanic activity is stronger for the sulfur contribution than the desert contribution for iron.

[76] Figure 6 is a growth curve of *Chlorella vulgaris* with various media; without Fe(-Fe, diamond) equivalent to HNLC, without Fe and with fresh 100% volcanic ash (V100, triangle) LNLC, without Fe and with mixture of 75% clay and 25% volcanic ash (C75, circle) LNHC, and JM medium with Fe (+Fe, square) HNHC.

[77] Figure 7 is a diagram illustrating that the carriers of the inorganic nutrient pool are winds and currents, which have seasonal variations.

Claims

- [Claim 1] A method of selecting an appropriate location for the large-scale sequestration of atmospheric CO₂ being configured that such a location should be not only as far from sources of volcanoes, earthquakes and boundaries of tectonic plates but also as close to sources of deserts.
- [Claim 2] The method of claim 1, wherein Fe-replete complex is configured to stay as long as possible within 100m surface ocean with aid of Fe-replete eco-friendly composite to avoid the chemical conversion of iron to iron sulfide and enhance phytoplankton digestion.
- [Claim 3] The method of claim 2, wherein the Fe-replete eco-friendly composite is with natural desert dust, clay, volcanic ash, mucilaginous cyanobacteria and agar.
- [Claim 4] The method of claim 2, wherein iron input for algal blooms is not bulk scale additions of direct iron or iron sulfate, but deploying natural clays or soils available nearby islands with possible content of iron in the range of 3.5 to 6wt%, as observed elsewhere in the Continents, along with volcanic ash desulfurized by rainfall and weathering for long time.
- [Claim 5] The method of claim 1, wherein four groups (HNLC, LNLC, HNHC, LNHC) of oceanic regions are on the basis of the relative degree of the accumulation rates of iron and sulfur.
- [Claim 6] The method of claim 1, wherein the deployment of Fe-replete composite is configured to be on the streamline of the Antarctic Circumpolar Current (~4km/h) in order to have a high momentum flux for efficient dispersion of Fe-replete composite on the ocean surface where diatom, copepods, krill and humpback whale stay together (~100m).
- [Claim 7] The method of claim 1, wherein the success of the large-scale iron fertilization is claimed by the return of the humpback whale if there were no humpback whale for long time before the iron fertilization.
- [Claim 8] The method of claim 1, wherein on-line monitoring for the successful iron fertilization is claimed by the simultaneous change of two groups; increase (chlorophyll, O₂, DO, DMS) and decrease (nitrate, phosphate, silicate, CO₂, DCO₂)
- [Claim 9] The method of claim 1, wherein the preferable locations for the large-scale iron fertilization are claimed as
- 1) Shag Rocks of South Georgia in Scotia Sea of the Southern Ocean,
 - 2) Bransfield Strait in Drake Passage of the Southern Ocean,
 - 3) west Iceland,

- 4) Mariana Islands/Guam of the U.S. Territory,
- 5) Hawaiian Islands,
- 6) North Pacific Subtropical Gyre.

[Claim 10] The method of claim 9, wherein the more preferable locations are claimed as 1)Shag Rocks, 2)Bransfield Strait and 3)west Iceland.

[Claim 11] The method of claim 10, wherein the most preferable location is claimed as "Shag Rocks".

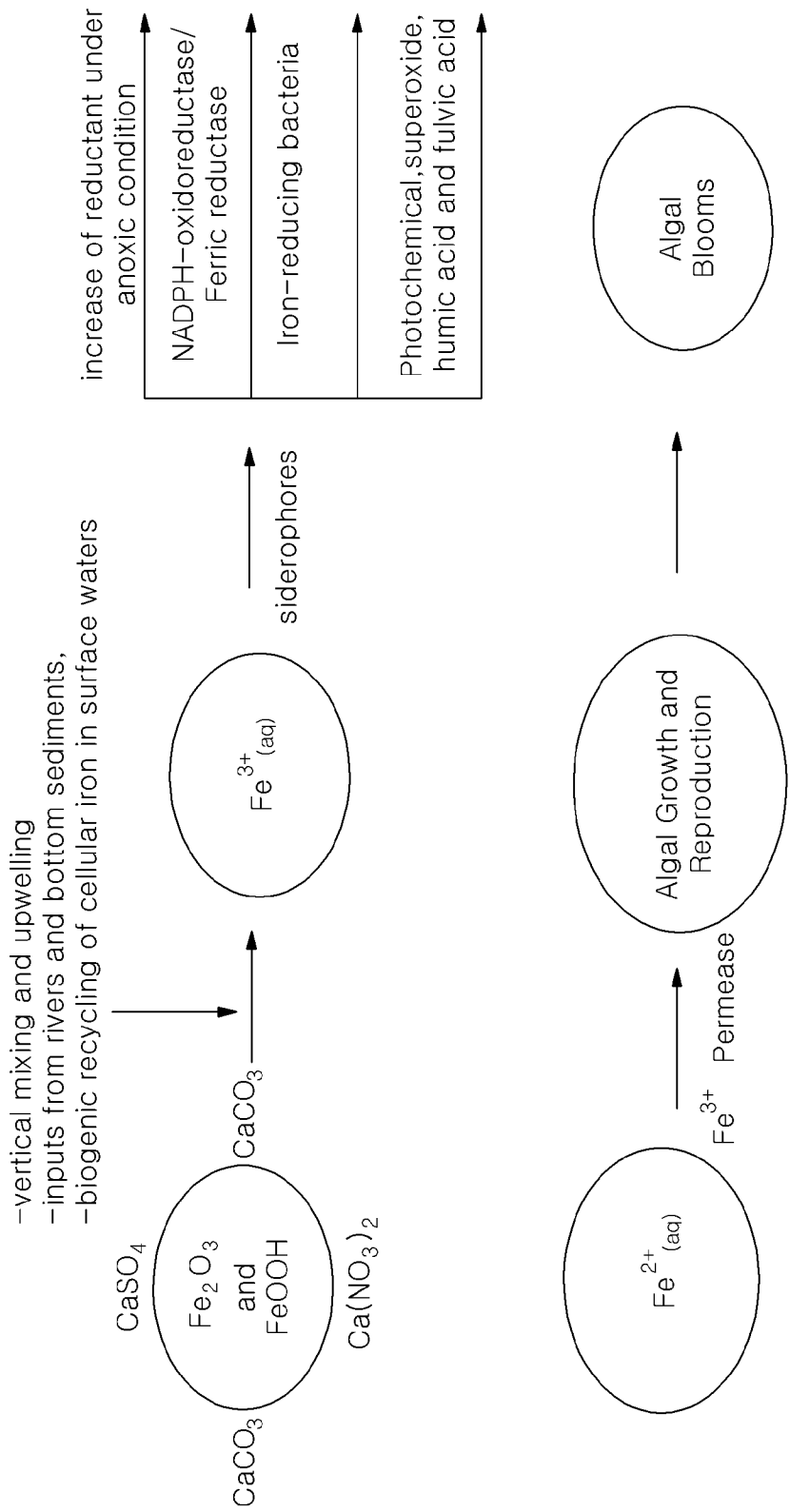
[Claim 12] The method of claim 1, wherein Grytviken of South Georgia in Scotia Sea is claimed as the base camp for the iron fertilization.

[Claim 13] The method of claim 8, wherein on-line monitoring of components are configured to be carried out at the fertilizing ships; one ship fertilizing the Fe-replete composite is located at the upward streamline of the ACC (Antarctic Circumpolar Current) while another ship monitoring the response of the iron fertilization by both of satellite (Chlorophyll-a, nitrate, DiMethyl Sulfide) and serial sensors (Chlorophyll-a, phosphate, silicate, iron, O₂, Dissolved Oxygen, CO₂, Dissolved Carbon Dioxide) is positioned at the downward streamline of the ACC.

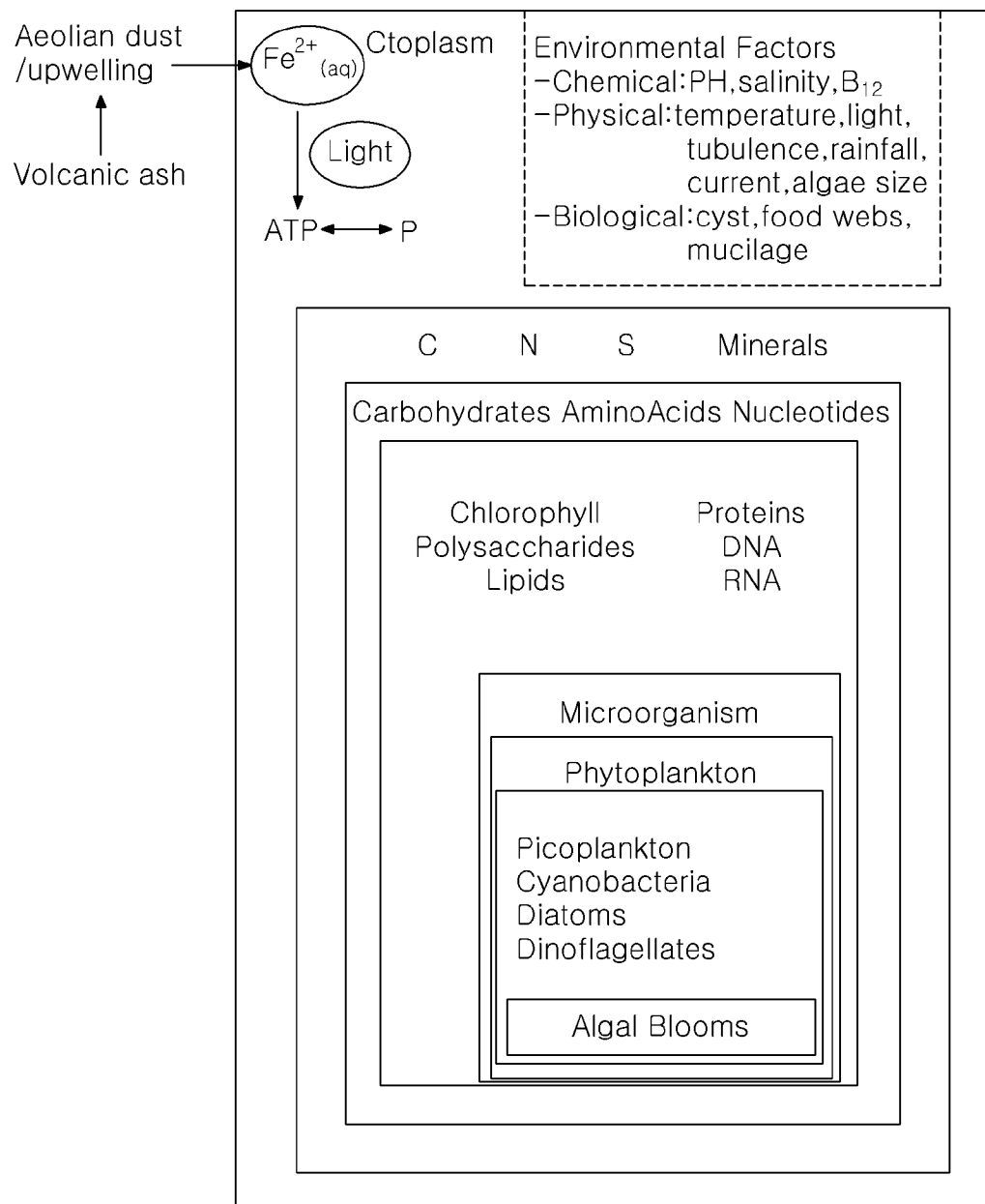
[Claim 14] The method of claim 5, wherein LNLC regions such as west Iceland, Mariana Island/Guam of the U.S. Territory, Hawaiian Islands and North Pacific Subtropical Gyre are configured to be temporally turned not only to LNHC regions with great hot fisheries but also the preferable locations for the large-scale iron fertilization to reduce the atmospheric CO₂.

[Claim 15] The method of claim 8, wherein the monitorings of chlorophyll, nitrate phosphate, and silicate concentrations after deploying the Fe-replete complex is configured to be made throughout the day and the night for the accurate estimation and prediction of algal blooms.

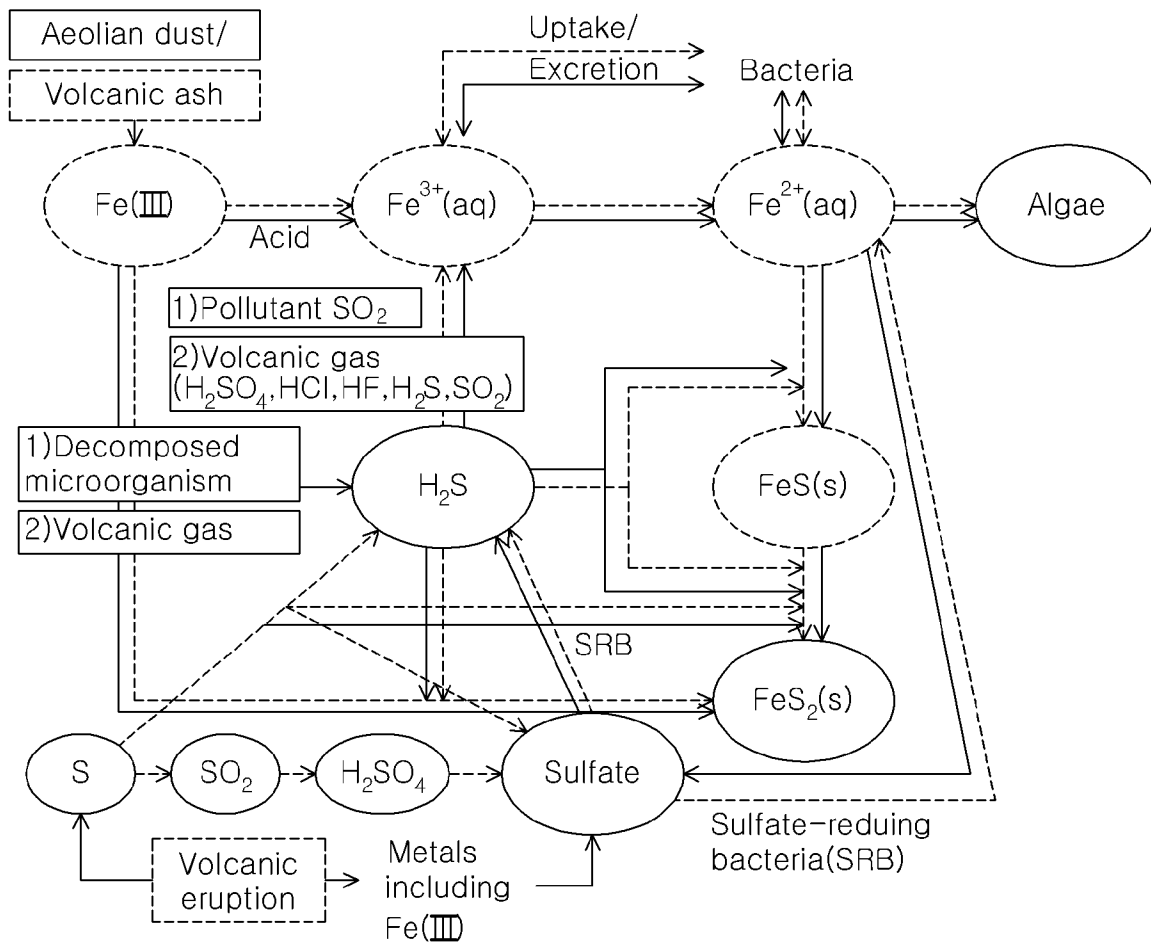
[Fig. 1]



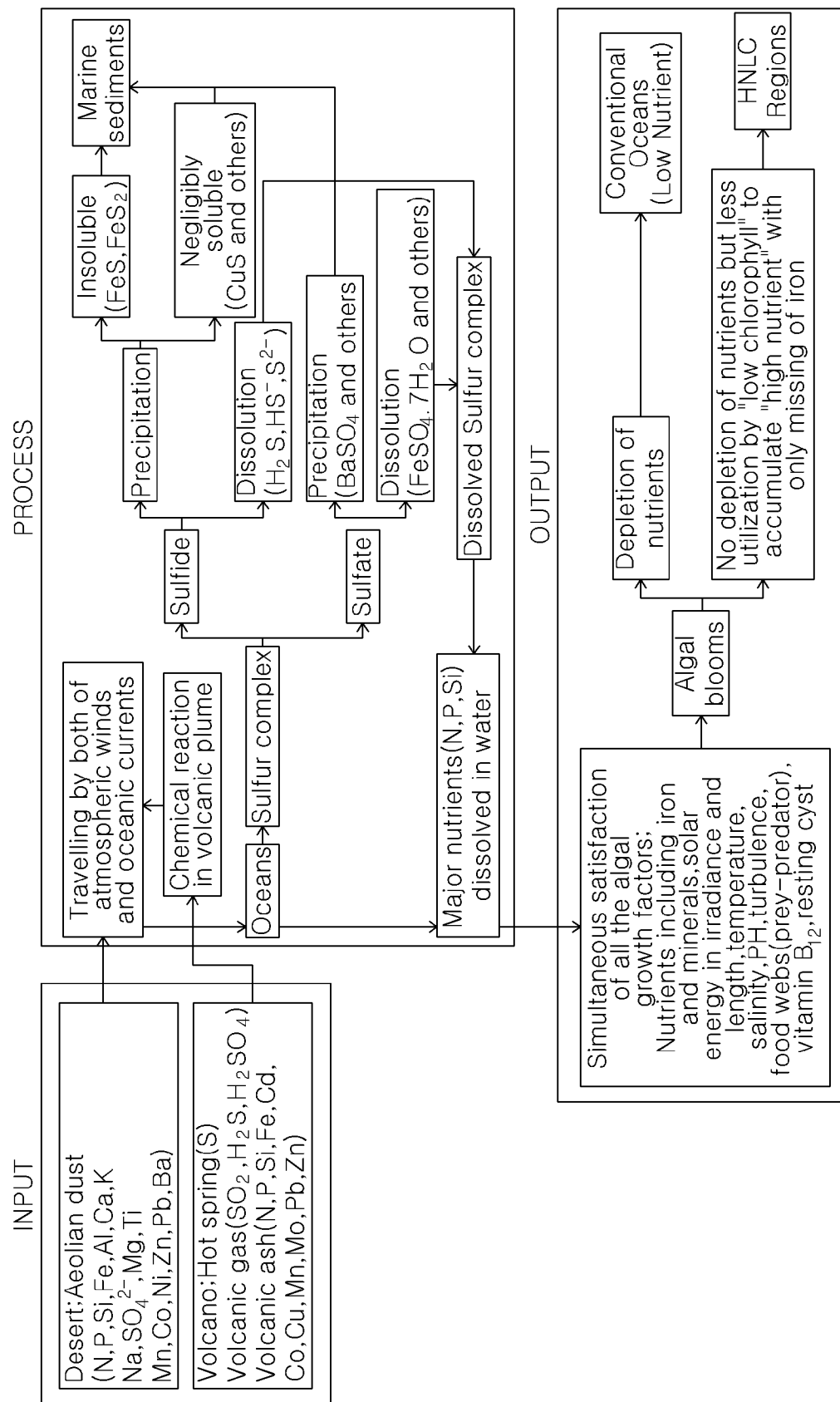
[Fig. 2]



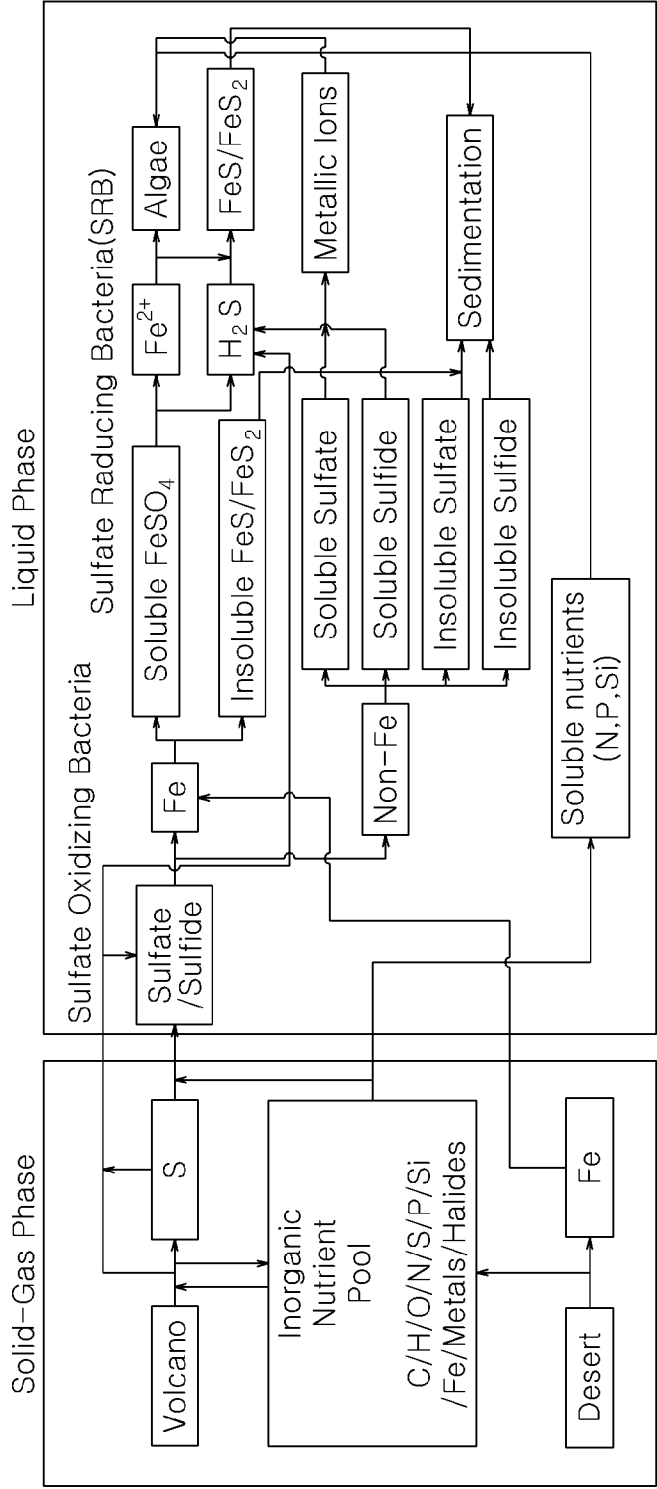
[Fig. 3]



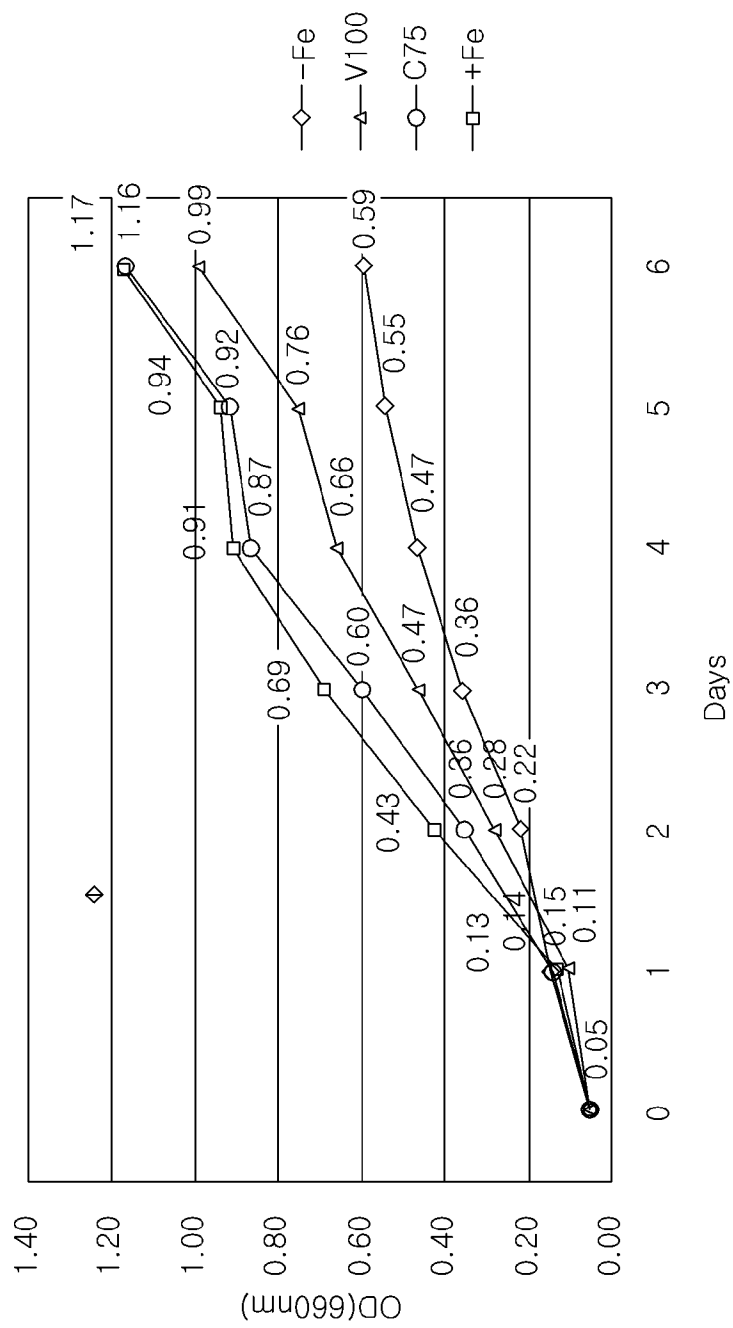
PROCESS



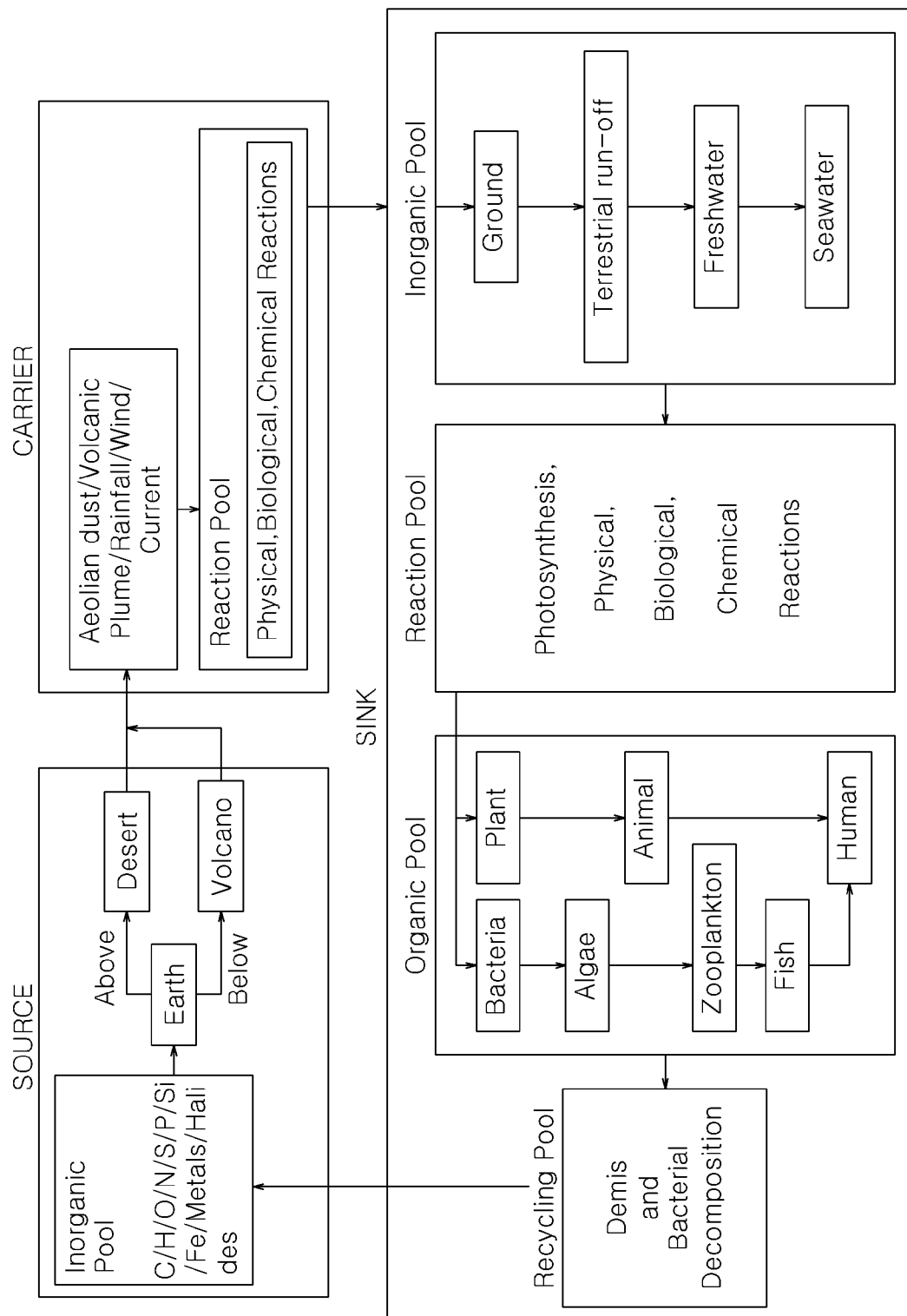
[Fig. 5]



[Fig. 6]



[Fig. 7]



PATENT COOPERATION TREATY

PCT

DECLARATION OF NON-ESTABLISHMENT OF INTERNATIONAL SEARCH REPORT
(PCT Article 17(2)(a), Rules 13ter.1(c) and (d) and 39)

Applicant's or agent's file reference PIB507115GLA	IMPORTANT DECLARATION	Date of mailing (<i>day/month/year</i>) 01 April 2016 (01.04.2016)
International application No. PCT/KR2015/007698	International filing date (<i>day/month/year</i>) 23 July 2015 (23.07.2015)	(Earliest) Priority date (<i>day/month/year</i>)
International Patent Classification (IPC) or both national classification and IPC B01D 53/62(2006.01)i		
Applicant G-LAND		

This International Searching Authority hereby declares, according to Article 17(2)(a), that **no international search report will be established** on the international application for the reasons indicated below.

1. ☐ The subject matter of the international application relates to:
 - a. ☐ scientific theories
 - b. ☐ mathematical theories
 - c. ☐ plant varieties
 - d. ☐ animal varieties
 - e. ☐ essentially biological processes for the production of plants and animals, other than microbiological processes and the products of such processes
 - f. ☐ schemes, rules or methods of doing business
 - g. ☐ schemes, rules or methods of performing purely mental acts
 - h. ☐ schemes, rules or methods of playing games
 - i. ☐ methods for treatment of the human body by surgery or therapy
 - j. ☐ methods for treatment of the animal body by surgery or therapy
 - k. ☐ diagnostic methods practised on the human or animal body
 - l. ☐ mere presentation of information
 - m. ☐ computer programs for which this International Searching Authority is not equipped to search prior art
2. ☒ The failure of the following parts of the international application to comply with prescribed requirements prevents a meaningful search from being carried out:

☒ the description
☒ the claims
☐ the drawings
3. ☐ A meaningful search could not be carried out without the sequence listing; the applicant did not, within the prescribed time limit:

☐ furnish a sequence listing in the form of an Annex C/ST.25 text file, and such listing was not available to the International Searching Authority in a form and manner acceptable to it; or the sequence listing furnished did not comply with the standard provided for in Annex C of the Administrative Instructions.

☐ furnish a sequence listing on paper or in the form of an image file complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it; or the sequence listing furnished did not comply with the standard provided for in Annex C of the Administrative Instructions.

☐ pay the required late furnishing fee for the furnishing of a sequence listing in response to an invitation under Rule 13ter.1(a) or (b).
4. Further comments:

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