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남극해 철 실험 전후의 N_2O 발생량 변화 연구

Investigation of variation in oceanic N_2O production by iron fertilization experiment

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제 출 문

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본 보고서를 “남극해 탄소저감 최적기능 환경특성 연구” 과제의 위탁연구 “남극해 철 실험 전후의 N_2O 발생량 변화 연구” 과제의 보고서로 제출합니다.

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보고서 초록

위탁연구과제명	남극해 철 실험 전후의 N_2O 발생량 변화 연구					
위탁연구책임자	김일남	해당단계 참여연구원수	4명	해당단계 연구비	50,000,000 원	
연구기관명 및 소속부서명	인천대학교 산학협력단 해양학과		참여기업명			
국제공동연구	상대국명 :		상대국연구기관명 :			
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1. N_2O 측정 시스템 구축
(1) 관련 논문 및 자료 확보를 통한 시스템 구축 사전 조사
(2) GC를 기반으로 한 Purge and Trap 방법의 N_2O 분석 장비 모식도 작성
(3) 전처리 시스템에 필요한 물품 조사 및 구매(Trap, solenoid valve, valco valve, fitting, sparger, loop 등등)

2. 철 비옥화 실험의 최적 시기 및 해역 선정
(1) 해색 위성 자료 중 엽록소 - a 농도와 표층수온 자료 분석
(2) 남극해 탄소 저감 후보지역(Weddell-Scotia Sea)에 대한 시・공간적인 해양 환경 변화 파악

3. 과거 Ocean Iron Fertilization 실험 리뷰 논문 투고
(1) 과거 OIF 실험 결과들에 대한 종합적인 토론을 통해 향후 남극해 철 실험을 위한 디자인 제시

색 인 어 (각 5개 이상)						
	한 글	아산화질소	분석 장치	남극해	해양환경	철 비옥화
	영 어	N_2O (nitrous oxide)	Analysis system	Southern Ocean	Ocean Environment/ Ecosystem change	Ocean Iron Fertilization

요 약 문

Ⅰ. 제 목

남극해 철 실험 전후의 N_2O 발생량 변화 연구

Ⅱ. 연구개발의 목적 및 필요성

이산화탄소 저감을 위한 남극해 철 비옥화 실험 전후의 해양 N_2O 발생량 변화 연구 및 인과 관계 규명

Ⅲ. 연구개발의 내용 및 범위

남극해 철 비옥화 실험에 따른 해양 환경 변화(N_2O 발생량 변화) 진단

Ⅳ. 연구개발결과

해수 중에 용존된 N_2O 기체 분석을 위한 원천 기술 확보

Ⅴ. 연구개발결과의 활용계획

남극해에서 철 비옥화 실험에 따른 해양 환경 변화(N_2O 발생)를 판단 할 수 있는 기초 자료 확보

S U M M A R Y

I. Title

Investigation of variation in oceanic N_2O production by iron fertilization experiment

II. Purpose and Necessity of R&D

To investigate variation in oceanic N_2O production by ocean iron fertilization in the Southern Ocean

III. Contents and Extent of R&D

Evaluation on the environment/ecosystem change (e.g., change in N_2O production, which is a strong greenhouse gas) by ocean iron fertilization experiment in the Southern Ocean

IV. R&D Results

Building of seawater N_2O gas analysis system

V. Application Plans of R&D Results

Obtaining of the fundamental data to determine whether ocean environment/ecosystem is changed to negative direction in terms of N_2O production by iron fertilization experiment in the Southern Ocean

목 차

제 1 장 서론

1.1 연구개발의 목적 및 필요성

아산화질소(N_2O)는 강력한 온실기체로 알려져 있다. N_2O는 대기 중에서 상대적으로 긴 체류시간(~120 년)을 가지고 대류권에서는 온실기체로서 작용을 하며, 성층권에서는 산화되어 오존을 제거하는 역할을 한다(IPCC, 2007). N_2O의 온실기체 효과는 CO_2의 300배의 달하는 것으로 알려져 있으며, 이로 인해 지구온난화를 가속화 시키는데 6% 기여하는 것으로 보고되었다(Rapson and Dacres, 2014).

N_2O는 미생물 활동에 의한 질산화(nitrification)와 탈질화(denitrification) 두 과정에 의해 생성되며(그림 1), 해양은 대기 중 N_2O의 주요 공급원으로 작용하며 총 연간 배출량(16-34 Tg N yr^{-1})의 약 20%(4-7 Tg N yr^{-1})를 차지한다(Nevison et al., 1995; Seitzinger et al., 2000; Bange, 2006). 산업혁명 이후, N_2O의 농도는 270ppb에서 320ppb로 약 20% 증가하였고, 이는 인간 활동에 의한 결과로 N_2O의 농도 증가가 가속화 되고 있다고 알려져 있다(그림 2).

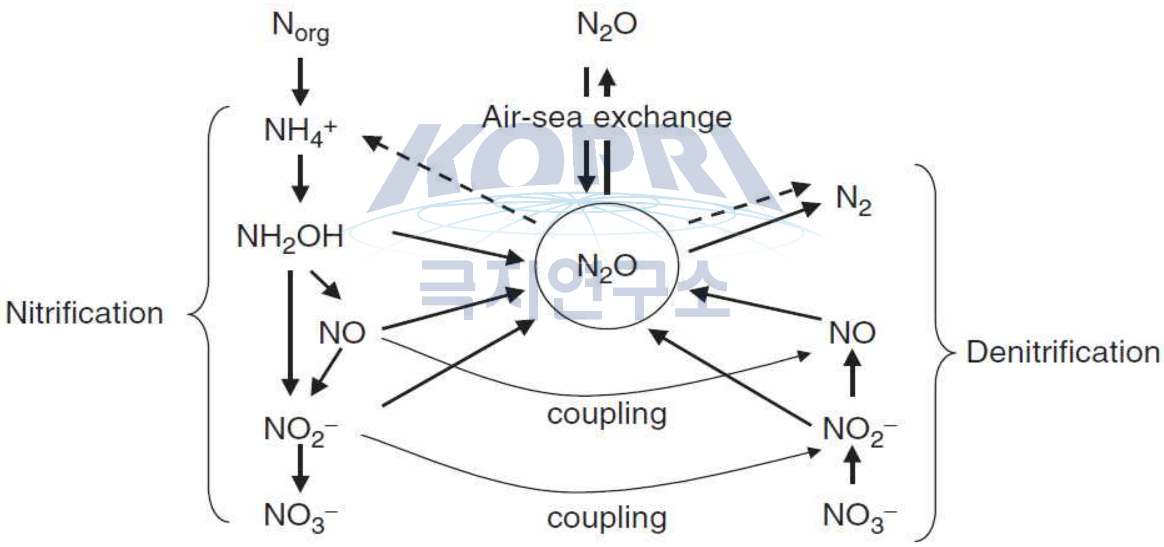


그림 1. 해양에서 질산화 및 탈질산화 과정에 의해서 N_2O 발생을 보여주는 모식도.

해양에서의 N_2O 발생은 주로 여름철 빈산소수괴가 강하게 발생하는 연안지역에서 높게 나타나는 것으로 알려져 있고, 연안지역의 N_2O의 배출량은 전체 해양 배출량의 60% 이상을 차지한다. 이로 인해 기존의 연구들은 연안지역에서의 N_2O 발생에 초점을 두어 진행되었다. 나아가 국제적으로 대양(태평양, 대서양, 인도양 및 북극, 남극해)의 장기조사(Hawaii Ocean Time-series, CCHDO, MEMENTO 등등)를 통하여 N_2O 발생량을 측정하고 이에 따른 환경변화를 이해하려는 연구도 진행되고 있다.

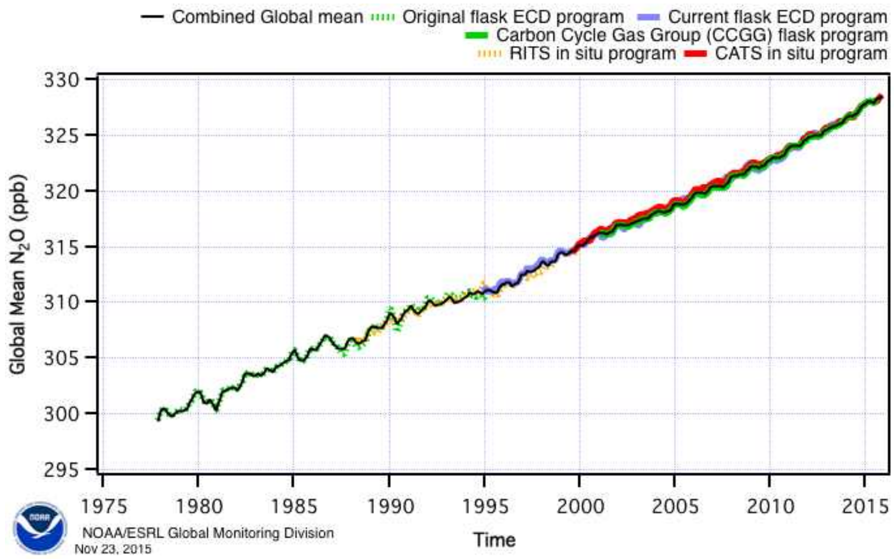


그림 2 연간 대기 중 N_2O 농도 변화(NOAA, 2015).

기후변화의 영향을 상쇄시키기 위한 일환으로 진행되는 해양의 철 비옥화 실험에 대한 영향으로 N_2O의 발생이 증가한다는 보고가 존재한다(그림 3, Fuhrman and Capone, 1991; Jin and Gruber, 2003; Law and Ling, 2001). 하지만 이 연구결과들과는 반대로 European Iron Fertilization Experiment(EIFEX)에서는 철 비옥화 실험으로 인한 해수 중 N_2O의 발생량이 증가하는 현상을 발견하지 못하였다(Walter et al., 2005). 이러한 상반된 결과는 해양 철 비옥화 실험에 따른 N_2O의 발생관계가 명확하지 않음을 나타낸다. 그러므로 철 비옥화 실험과 N_2O 발생의 인과관계를 밝히기 위해 남극해 철 비옥화 실험 전후의 해수 중 N_2O의 발생량 변화관찰이 필요하다. 해수 중 N_2O 분석 가능한 장비 개발을 통해 원천 기술을 확보하고 철 실험에 따른 N_2O 발생량 변화에 대한 본 연구는 국내에서 전무후무한 사례로 도전적이고 진취적인 연구이다.

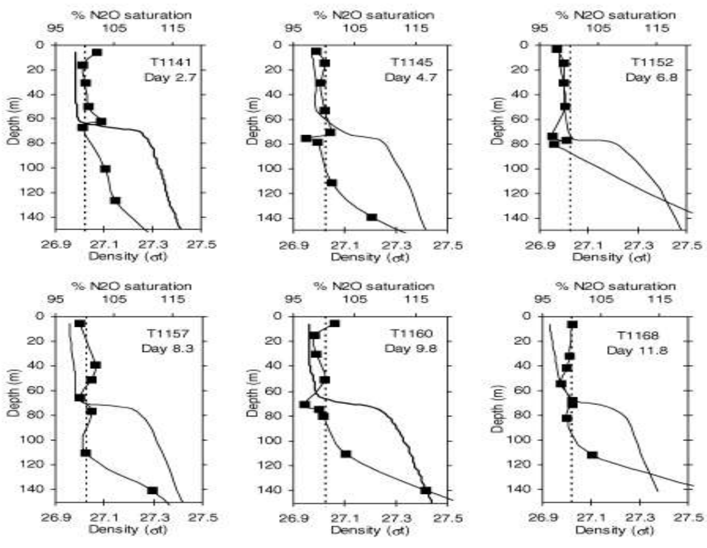


그림 3 수심 150m 의 수직 프로파일. 점선은 100% N_2O 포화도, 검은네모는 N_2O 포화 %, 실선은 포텐셜밀도를 나타냄(Law and Ling, 2001).

제 2 장 국내외 기술개발 현황

2.1 측정 기술

해양의 용존 N_2O의 측정은 크로마토그래피, 광학 및 전류를 이용한 방법(Chromatographic, optical and amperometric) 등과 같이 크게 세 가지로 분류되어 사용되어 지고 있다(표 1, Rapson and Dacres, 2014). 보편적으로 사용되고 있는 ECD detector를 이용한 GC 분석 방법은 다른 분석 방법에 비해 비용이 적게 들고 많은 양의 자료를 비교 분석 가능하며, 수집이 용이한 장점을 가지고 있다. 이러한 장점으로 본 연구에서도 GC를 이용한 분석 방법을 채택하였다.

표 1. N_2O 측정을 위한 이용 가능한 분석 기술(Rapson and Dacres, 2014).

	Sensitivity	Advantages of technique	Disadvantages of technique	
Chromatography				
Electron Capture Detector	30 ppb LOD Precision: 0.18–0.4 ppb	Lower cost Widely used, allowing easy data comparisons If linked to IRMS, isotope analysis can be carried out	Non-continuous Frequent calibration required Drift means reference needs to be run every 3 samples Long run time (~5 min)	[52]
Optical methods				
FTIR	Precision: 0.1 ppb (1 min)	Continuous measurements Lower calibration requirements	High cost of instruments Low brightness of light source	
	0.03 ppb (10 min)	Broadband spectrum allowing the measurement of multiple components and spectra can be reanalyzed	Slower measurements compared to lasers	[69,78]
		Direct detection of isotopomers with the same molecular mass Mid IR used at atmospheric pressure Portable	Analysis of data can be more complicated	
Laser absorption spectroscopy				
Lead Salt Lasers	Precision: <1 ppb in 5 sec	Allows rapid and highly sensitive measurements	Cryogenic cooling required	[80]
		Lower interference from other trace gases	Narrowband, can only measure a single species or pair per laser Low pressure required Expensive	
Quantum Cascade Lasers	Precision: 0.05 ppb in 1 Hz	No cryogenic cooling required making lasers more portable	Spectral quality not as high as Lead Salt Lasers	
		Higher power than lead salt lasers giving a higher signal to noise ratio and faster measurements Can be linked with high finesse optical cavities such as CRDS and ICOS Carry out isotopic analysis without pre-concentration	Narrowband, can only measure a single species or pair per laser Low pressure required Expensive	[49]
Amperometric				
Microsensor	22 ppb LOD	Low cost	Sensor drift, therefore not suitable for long term monitoring	[111]
		Extremely portable	Only dissolved N_2O can be measured	

2.2 국내외 기술 동향 및 분석 기술 필요성

해수 중 용존된 기체를 추출해내는 방법에는 headspace, purge and trap, solid phase micro-extraction 등이 있다. 본 연구에서는 purge and trap 에 기초하여 Gas chromatography(GC)를 이용한 장비를 구축 및 활용할 계획이다. 이 기술은 시료가 이동상과 고정상 사이를 흐르면서 trap에 의해 저온 흡착 되고 고온에서 탈착되어 GC - ECD(전자포획검출기)를 통해 정성 및 정량 분석되는 원리를 이용하며(Sara et al., 2012), 국내에서는 이러한 분석 시스템이 장착 된 곳이 외국에 비해 적기 때문에 본 연구를 위한 최적화된 분석 기술 구축이 요구 된다. 대표적으로 국외의 하와이 대학과 국내의 포항공과대학(그림 4)에 분석 장비가 구축되어 해양의 N_2O 연구를 주도적으로 진행하고 있다.

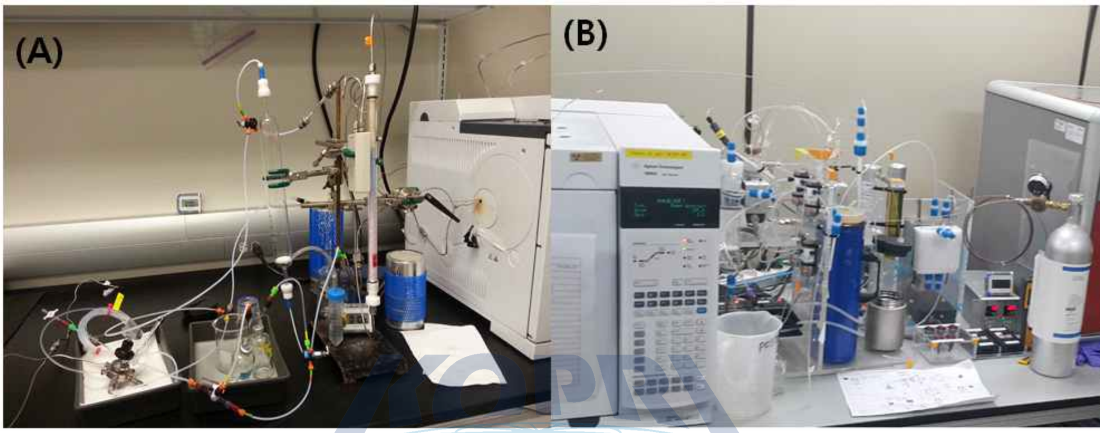


그림 4 국내외 N_2O 분석 장비 시스템. (A) 하와이 대학교 시스템, (B) 포항공과대학교 시스템.

제 3장 연구개발수행 내용 및 결과

3.1 N_2O 분석 시스템 구축

남극해 철 비옥화 실험 전후의 N_2O 발생량 변화를 알아보기 위한 해수의 용존 기체 N_2O의 측정을 위해 최적화 된 분석 시스템 구축

- 전처리 장치 모식도 설계
- 장비 조사 및 구매
- 시스템 구축

3.1.1 진행상황 및 세부내용

- 전처리 장치 모식도 설계

연구목적에 최적화된 시스템 구축을 위해 포항공과대학교의 N_2O 분석 장비를 기초로 하여 보완된 purge and trap 방법의 분석 장비 모식도를 작성하였다(그림 5).

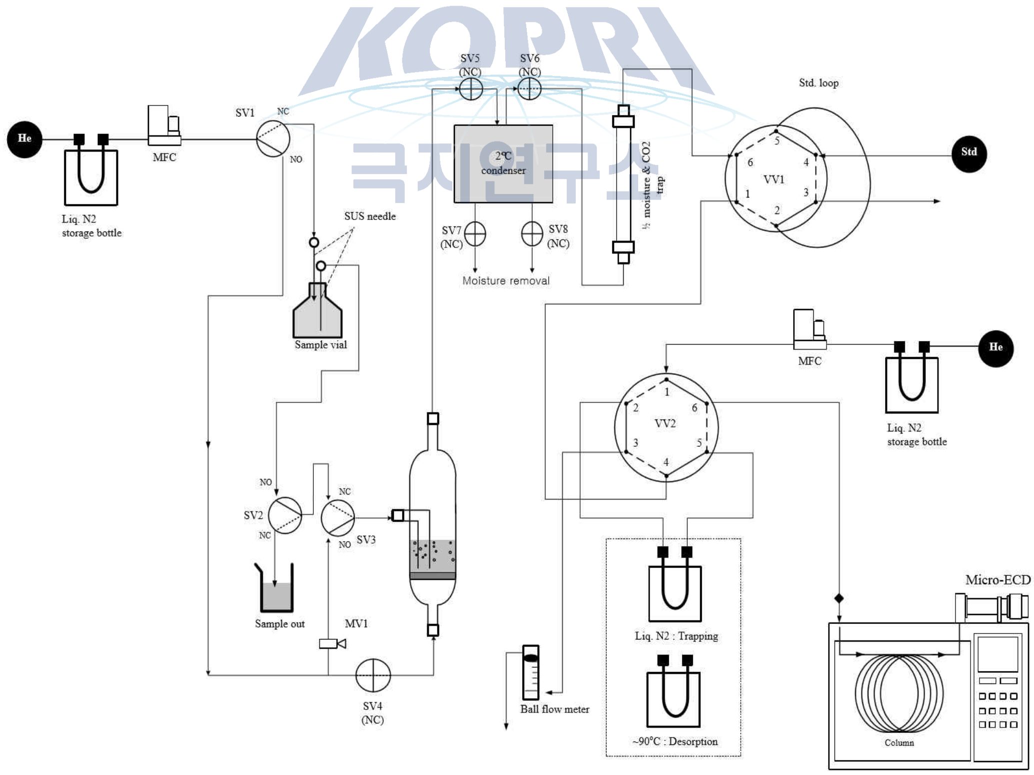


그림 5 N_2O 분석 장비 전체 모식도.

- Purge and trap 방법

① 퍼지 단계

분석에 필요한 일정량의 시료를 스파저(sparger)에 옮긴 후, 스파저의 비활성기체(inert gas) 주입을 통한 폭기 과정을 거쳐 용존 기체를 추출하는 단계이다.

③ 흡착 단계

앞서 스파저를 통해 분리된 용존 기체들이 이동상기체(Carrier gas, He)를 통해 트랩으로 옮겨진다. 옮겨진 기체들은 저온에서 트랩에 흡착 된다.

③ 탈착 단계

앞서 두 과정에 의해 시료로부터 분리된 용존 기체는 트랩에 흡착되어 있는 상태에서 순간적으로 트랩에 고온의 열을 주어 흡착되어 있는 용존 기체들을 탈착 시켜 캐리어가스와 함께 GC로 주입. GC로 주입된 용존 기체들은 ECD를 통해 정성/정량 분석이 이루어지며 그 중 N_2O를 분석한다.

● 장비 조사 및 구매

- N$_2$O 분석 시스템 구축을 위한 장비(Trap, condenser, moisture removal column, Solenoid valve, Valco valve, line 등등) 조사 및 구매를 진행하였다(표 2).

표 2 N$_2$O 분석 장비 구축을 위해 필요한 물품 목록

	Model	제조사	Product NO.	수량	비고
1	PEEK loop for cheminert valve 20uL	VICI	CFSL20PK	1	Low Pressure Injector - 1/4-28 fittings
2	PEEK loop for cheminert valve 100uL	VICI	CFLS100PK	1	Low Pressure Injector - 1/4-28 fittings
3	PEEK loop for cheminert valve 1mL	VICI	CFSL1KPK	1	Low Pressure Injector - 1/4-28 fittings
4	100T isolation valve, 3-way type	Bio-chem	100T3MP12-62	6	12V DC, 0.062" orifice, Cv - 0.028
5	Sus 1/8" 6 port valco valve	VICI	ED6UWE	2	GC Sampling/Switching Valves - 1/8"fitting, 0.75 mm bore
6	Sample Loop for 1/8" Valco Injecctors with 0.75 mm ports (20uL)	VICI	SL20UW	1	
7	Sample Loop for 1/8" Valco Injecctors with 0.75 mm ports (50uL)	VICI	SL100UW	1	
8	Sample Loop for 1/8" Valco Injecctors with 0.75 mm ports (1mL)	VICI	SL1KUW	1	
9	SUS Swagelok Tube fitting, Low Dead Voloume Union, 1/16 in. Tube OD	Swagelok	SS-1F0-6GC	2	capillary column & 1/16 연결용
10	PFA Swagelok Tube Fitting, Reducing Union, 1/2 in. Tube Fitting x 1/4 in. Tube fitting	Swagelok	PFA-820-6-4	4	Moisture trap & line 연결
11	PFA Swagelok Tube Fitting, Reducing Union, 1/4 in. x 1/4 in. Tube OD	Swagelok	PFA-420-6-2	15	Moisture trap, glasswar & line 연결
12	SUS Swaglok 1/8 Union 1/8 in. Tube OD	Swagelok	SS-200-6	4	trap 연결용
13	316 SUS Swagelok 1/8 in. Front Ferrule	Swagelok	SS-203-1	3	
14	316 SUS Swagelok 1/8 in. Back Ferrule	Swagelok	SS-204-1	3	
15	SUS Swagelok Tube Fitting, Reducing Union, 1/8 in. x 1/16 in. Tube OD	Swagelok	SS-200-6-1	4	trap 연결용
16	SUS 1-Piece 40 Series Ball Valve, 0.2 Cv, 1/8 in. Swagelok Tube fitting	Swagelok	SS-41GS2	3	Standard gas on/off
17	Ball Flow meter with Flow Controller	KOFLOC	RK2503F	1	He purging 측정용
18	Luerlock type sus needle (130mm length)	HAMILTON	7751-01	5	10 guauge, Metal Hub NDLY, point style 5 or AS, 6/PK
19	N2O standard gas (Nitrous oxide in nitrogen)	SIGMA-ALDRICH	Scott Gas, T446-48	1	10ppm, cylinder of 48 L, analytical standard
20	N2O standard gas regulator (Model 24 Single-Stage Regulator)	SIGMA-ALDRICH	16-05-124 SP165	1	for use with CGA-165 for SCOTTY 48 cylinder
21	Drierite (>98% CaSO4, >2% CoCl2)	Drierite	24001	1	1 lb, 10-20 mesh
22	Liquid N2 bottle_~2L(Dewar Flask)	SIGMA-ALDRICH	PO.8621	1	저온 흡착용
23	Liquid N2 bottle_~4L(Dwar Flask)	SIGMA-ALDRICH	PO.8642	1	carrier gas의 trace materials 제거
24	Switch on/off	Autonics	S2TR-P3	10	
25	1/8 PFA tube 10m	Swagelok	PFA-T2-030-100	1	
26	Sparger	Aceglass	Z408727	2	해수 폭기 용
27	Sparegr 용 frit	Aceglass		3	
28	1/2 inch, 20cm straight tube	Aceglass		3	chemical dryer & adsorbor packing, 업체 주문제작
29	1/4 inch, 10cm straight tube	Aceglass		3	업체 주문제작
30	condensor	Aceglass		1	업체 주문제작
31	DC power supplier (SMPS) 12V 5A	Aceglass	MSF60-12	2	
31	DC power supplier (SMPS) 12V 2A	화인선트로닉스	MSF25-15	2	
32	온도 조절기 on/off 제어	Autonics	TZN4W Series	1	
33	8ft Porapack Q 60/80 in Ni	Agilent(GC Column	G3591-82137	1	trap
34	장비 거치대			1	주문제작

● 시스템 구축

- 전처리 시스템 장비 특성상 해외에서 구입되는 장비가 대부분이므로 구매 및 장비 도착 지연으로 인한 시스템 구축 지연
- 현재 보유한 장비를 토대로 시스템 구축을 진행 중이며, 17년 2월 구축 완료 예정.

3.2 해색 위성 분석

3.2.1 해색 자료의 특성

해색(Ocean color) 위성은 가시광선 스펙트럼 영역에서 입사한 태양광이 해수 밖으로 나오는 반사 스펙트럼을 측정하는 위성으로, 전 지구적으로 해양의 일차생산자인 식물플랑크톤의 생물량 및 일차생산력을 추정하기 위해 개발되었다. 해색위성 센서는 최초로 1978년부터 9년간 미국 항공우주(NASA)의 Nimbus-7 에 탑재되어 운영되었던 CZCS (Coastal Zone Color Scanner)를 시작으로 1990년대 후반부터는 일본의 ADEOS위성에 탑재된 OCTS (Ocean Color & Temperature Sensor), 미국 NASA의 SeaWiFS (Sea-viewing Wide Field- of-View Sensor), MODIS (Moderate Resolution Imaging Spectroradiometer), VIIRS (Visible and Infrared Imager/Radiometer Suite) 등이 차례로 개발되어 지난 30년 동안 지구의 탄소 순환 및 기후온난화의 측면에서 전 지구적인 해양의 역할을 이해하는 것을 가능하게 해왔다.

과거 중간규모(mesoscale)의 인위적인 철 비옥화 실험은 남극해를 포함한 HNLC (High Nutrient Low Chlorophyll) 지역에서 평균 약 24일의 기간 동안 수행되었는데, 철을 추가함에 따른 나타나는 생물학적 반응은 실험기간보다 오랫동안 지속되어 약 24일의 실험기간만으로는 인위적인 철을 추가함에 따른 생물학적 반응에 대해 완전히 이해하는데 제한이 있었다 (Abraham et al., 2000). 그러나 적도 태평양에서 수행된 IronEx 실험을 제외한 모든 실험이 해색위성 시대(1998년 이후)에 수행되었는데, 실험에 비해 상대적으로 시공간적 제약이 적은 해색위성자료의 사용은 인위적인 철 추가에 따른 생물학적 반응을 엽록소-a 농도의 자료를 토대로 시간에 따른 확인을 가능하게 할 뿐만 아니라 철이 해류에 의해 퍼져나가는 patch의 크기 및 모양까지도 확인할 수 있게 하였다(Coale et al., 2004; Westberry et al., 2013). 추후 해색자료를 바탕으로 한 일차생산의 추정은 철 비옥화 실험에 의한 시간에 따른 생물학적 펌프(biological pump)의 효과를 이해하는데 중요한 자료를 제공할 것으로 기대된다.

1차 년도에는 해색위성 자료 중 식물플랑크톤의 생물량을 대표하는 엽록소-a 농도와 물리적 현상을 대표하는 표층수온의 분석을 토대로 남극반도 탄소 저감 후보지역에 대한 시공간적인 해양 환경의 변화를 파악하여 2차 년도에 남극해 철 실험을 위한 eddy의 발생지역을 찾고 최적의 시기 및 해역을 선정하는데 필요한 자료를 제공하고자 한다.

3.2.2 자료 처리 방법

1차 년도에서는 접근이 용이한 저해상 자료 수준(Level-3)의 해색 위성 자료를 이용하여 남극반도 탄소 저감 후보지역을 포함하는 Weddell-Scotia Sea (59-65°S, 45-65°W)의 시공간별 해양 환경의 특성을 조사하였다(그림 6). 분석에 사용된 자료는 미국의 NASA OBPG (Ocean Biology Processing Group)의 MODIS Aqua (R2014.0)로부터 산출된 엽록소-a 농도와 표층수온 자료로 각 자료는 4 km의 공간해상도를 갖는 Mapped 월별 합성자료였다(http://oceandata.sci.gsfc.nasa.gov). 엽록소-a 농도는 OC3M (Ocean chlorophyll three-band algorithm) 알고리듬으로부터 추정된 자료이며(O'Reilly et al., 2000), 표층수온자료는 열적외선(11 μm)에 기반한 알고리듬으로부터 추정된 자료(Franz, 2006)로 2002년 7월부터 2016년 6월까지의 자료를 분석에 사용하였다.

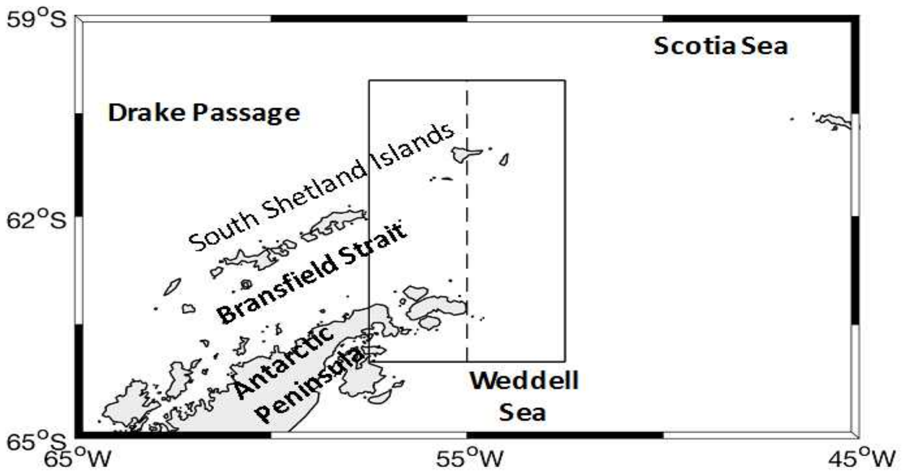


그림 6 남극반도 탄소 저감 후보지역을 포함하는 Weddell-Scotia Sea (59-65°S, 45-65°W). 검은색 실선 박스는 탄소 저감 후보지역을 나타냄.

3.2.3 결과 분석

3.2.3.1 엽록소 농도 자료의 특성

MODIS 자료로 부터 추정된 2002년 7월부터 2016년 6월까지의 엽록소 농도 자료에 대해 히스토그램(histogram)을 이용하여 자료의 전체적인 특성을 파악하였다(그림 7). 엽록소 농도 자료는 로그 분포를 하고 있으나 오른쪽으로 치우친 분포를 하고 있으며, 평균은 0.378 mg $^{-3}$로 중앙값 0.238 mg $^{-3}$보다 큰 값을 보였다.

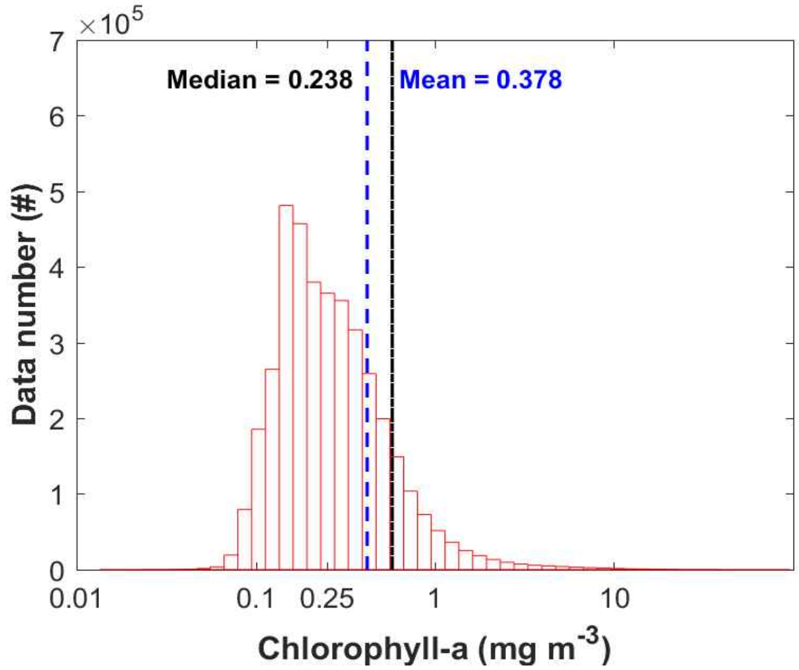


그림 7 엽록소-a 농도의 histogram.

3.2.3.2 평균 엽록소 농도 자료의 공간 분포

공간적으로 전 기간에 대해 평균한 엽록소-a 농도는 남극 반도 부근에서 높은 농도를 보이는데, Weddell Sea에서 약 2 mg $^{-3}$이상으로 높고 South Shetland islands를 둘러싼 해역에서 0.6 mg $^{-3}$로 다른 해역보다 높은 값을 나타내며, 특히 59-62°S 사이의 Drake Passage에서 가장 낮은 농도 분포를 보였다(그림 8). 표준편차는 평균 엽록소-a 농도와 공간적으로 비슷한 패턴을 보였다(그림 9).

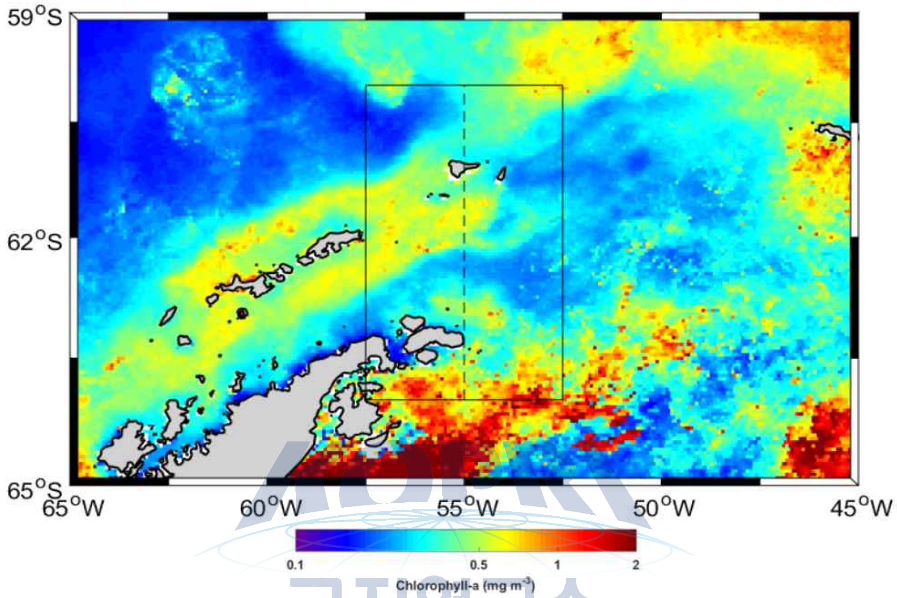


그림 8 평균 엽록소-a 농도.

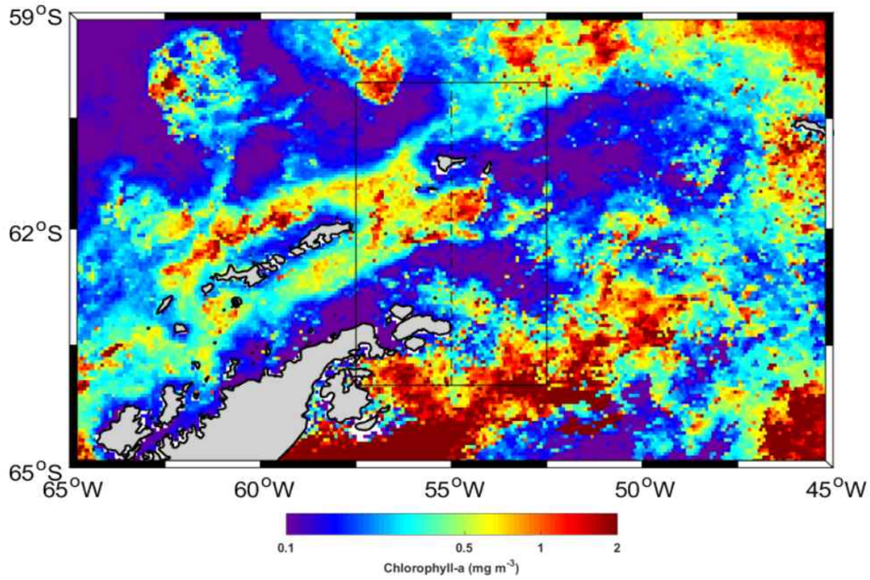


그림 9 엽록소-a 농도의 표준편차

3.2.3.3 평균 표층 수온 자료의 공간 분포

공간적으로 전 기간에 대해 평균한 표층 수온의 분포는 Bransfield Strait을 기준으로 극으로 갈수록 표층수온이 0℃이하로 낮은 값을 나타내며, 북쪽으로 갈수록 상대적으로 1℃ 이상의 높은 값을 보였다(그림 10). 전 기간에 대한 표준편차는 약 1℃ 로 공간적으로 비슷한 값을 보였다(그림 11).

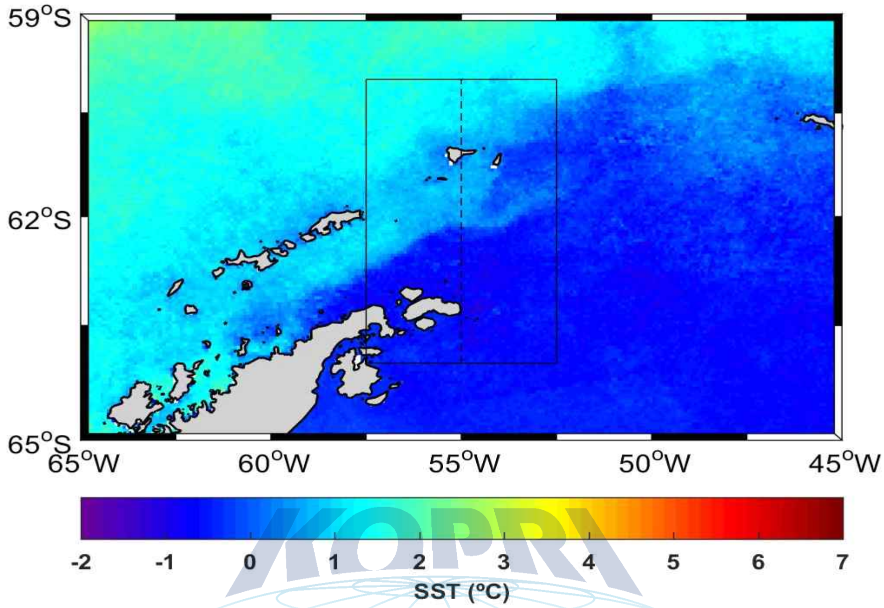


그림 10 평균 표층 수온.

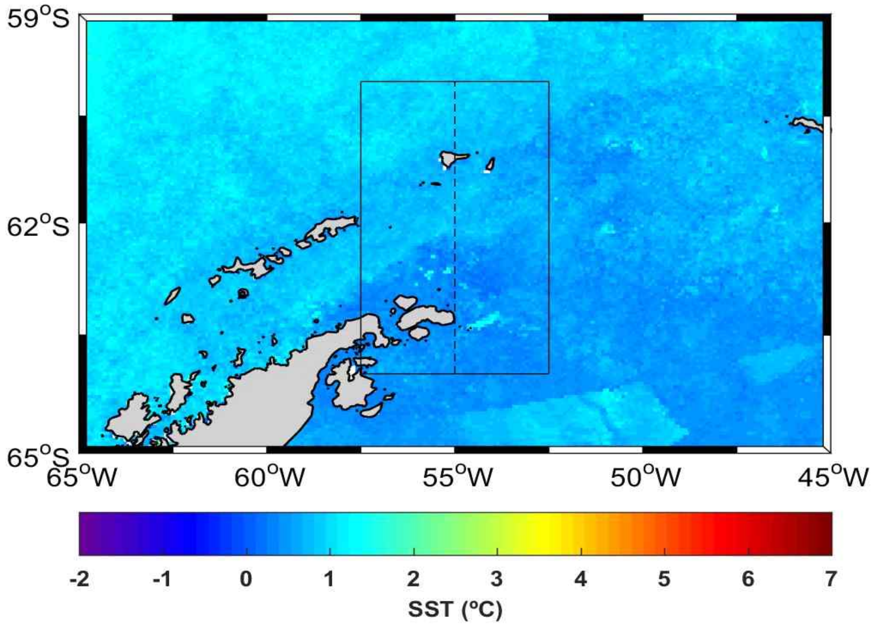


그림 11 표층 수온의 표준편차.

3.2.3.4 연도별 엽록소 농도

연도별 평균 엽록소-a 농도는 2006년에 0.295 mg^{-3}로 가장 높고, 2003년에 0.275 mg^{-3}로 2002년을 제외한 연도 중 가장 낮았다(그림 12). 공간적으로 각 연도에 대한 anomaly 분포를 살펴보면 2006년에 특히 South Shetland islands를 둘러싼 해역에서 높은 농도를 나타냈는데, 두 번째로 전 영역에 대한 평균 엽록소-a 농도가 높았던 2005년의 경우에는 Scotia Sea 쪽에서 높은 농도를 보였다. 2011년도와 2015년도에는 다른 해역에 비해 Drake Passage 해역에서 높은 농도의 값을 보였다(그림 13). 2016년도에는 엽록소-a 농도가 특히 Bransfield Strait해역에서 높았다.

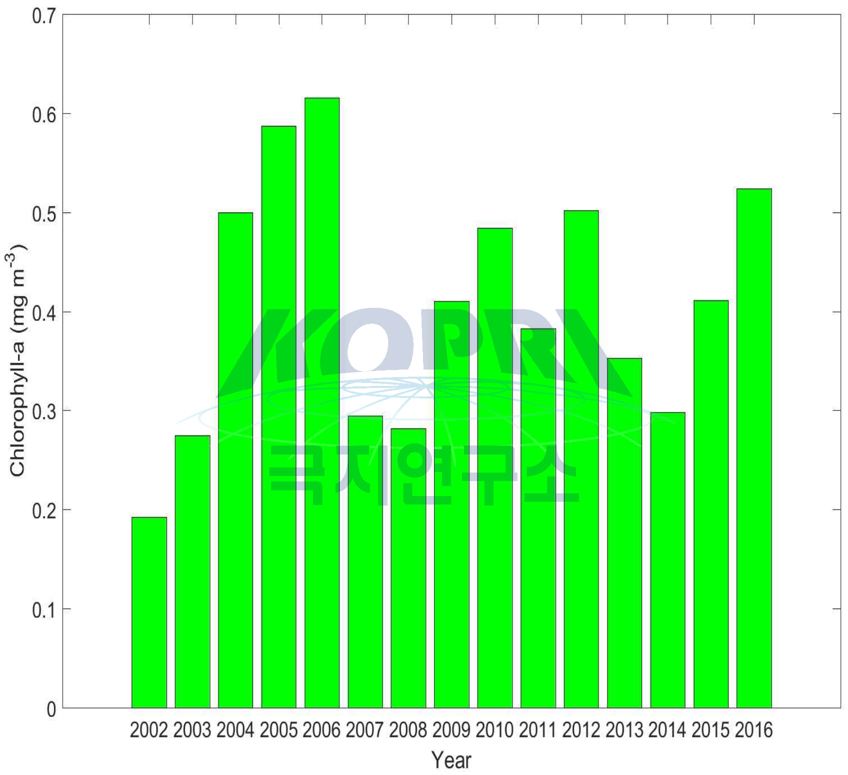


그림 12 연도별 평균 엽록소-a 농도.

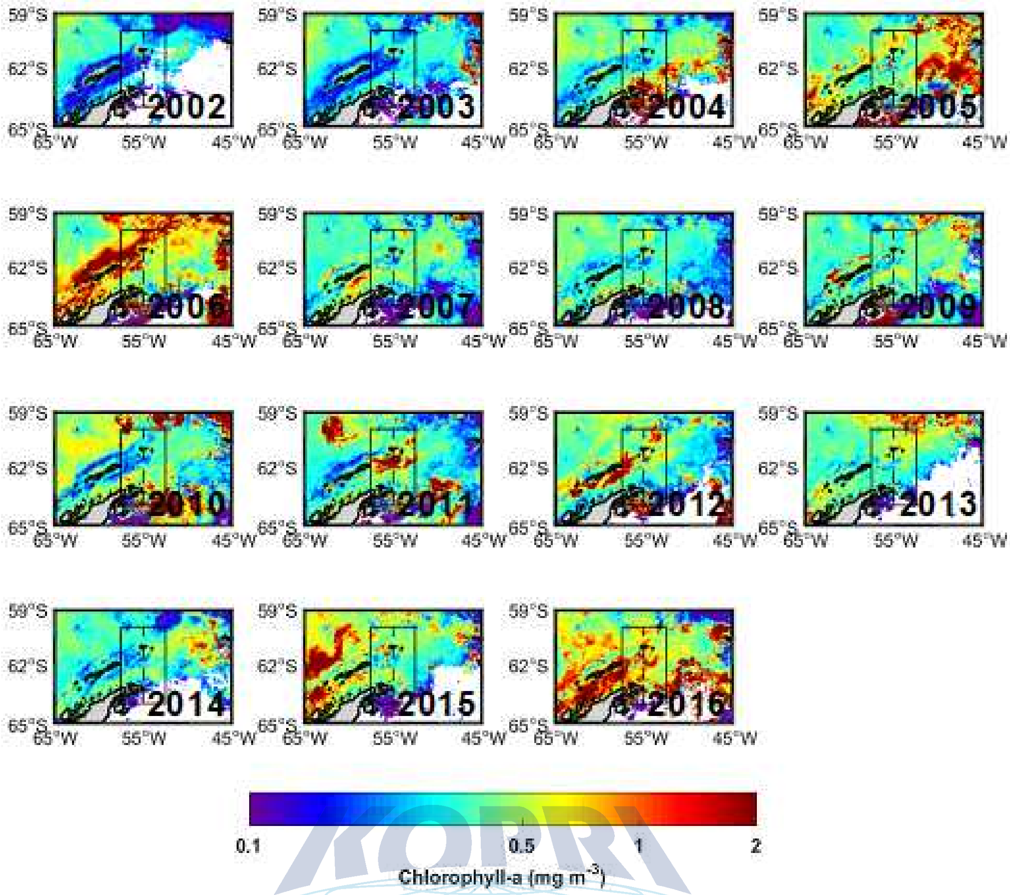


그림 13 연도별 엽록소-a 농도의 anomaly 분포.

3.2.3.5 연도별 표층수온

연도별 평균 표층 수온(그림 14) 및 anomaly 공간분포(그림 15)를 살펴보면, 2006년에 1.3°C로 가장 높은데, 2006년도 표층수온 anomaly는 전 영역에 걸쳐 평균값에 비해 높은 값을 보이고 있었다. 2002년(9-12월 자료)과 2016년(1-4월 자료)의 경우 평균 표층수온이 -0.1°C과 0.06°C로 가장 낮았으며, 공간적으로는 특히 Drake Passage해역에서 낮은 anomaly의 값을보였다. 반면 2003, 2007년에는 Drake Passage해역에서 높은 anomaly의 값을 보였고, 2009년에는 South Shetland islands를 둘러싼 해역에서 높은 anomaly의 표층수온을 보였다.

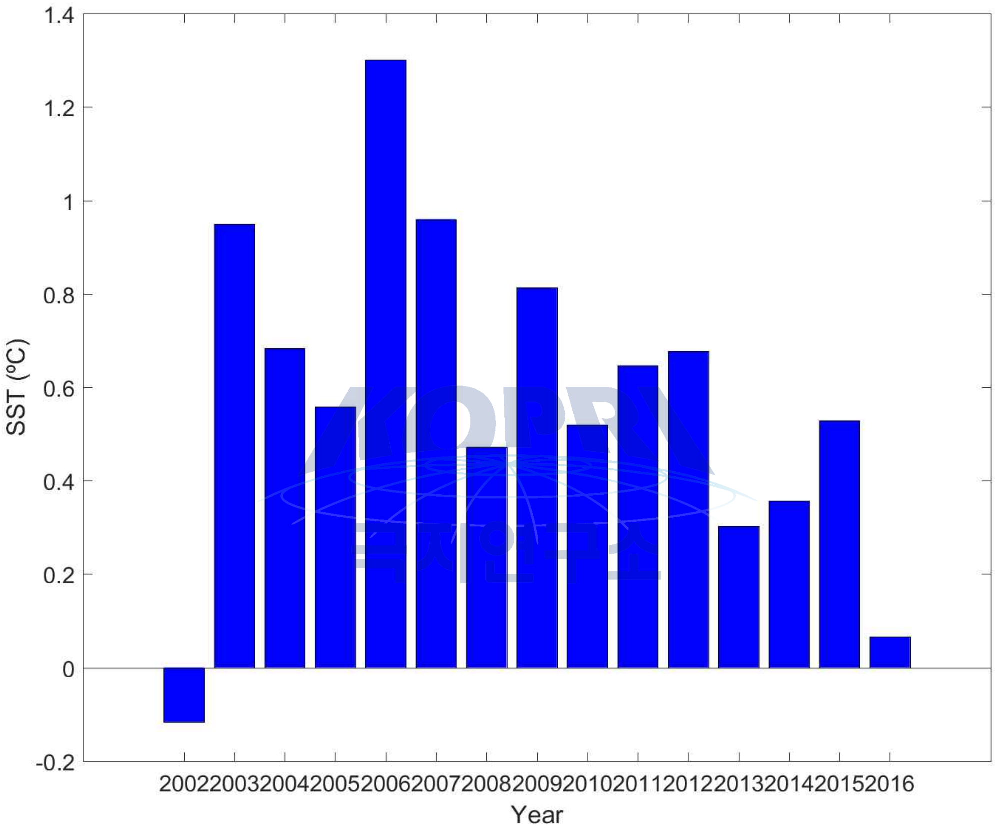


그림 14 연도별 평균 표층수온.

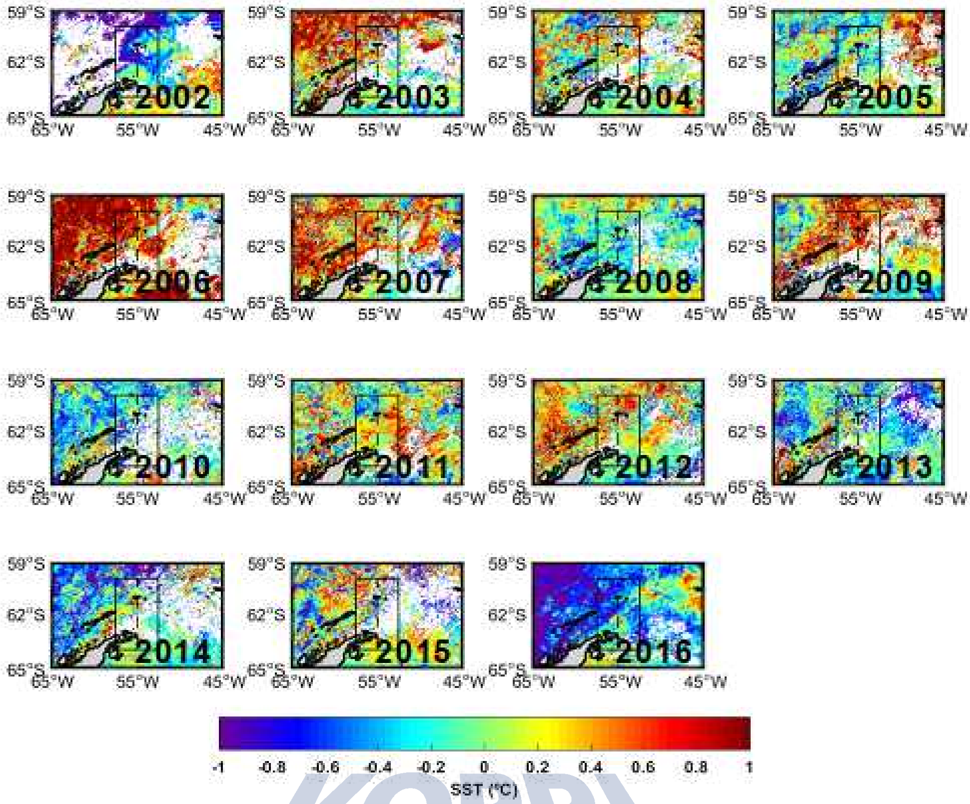


그림 15 연도별 표층수온의 anomaly 분포.

3.2.3.6 월별 평균 엽록소 농도 분포

월별 평균 엽록소-a 농도는 5월부터 7월까지 관측되지 않았으며, 9월에 가장 낮고(0.175 mg m^{-3}),1월에 가장 높은 농도를 보였다가(0.584 mg m^{-3})다시 낮아지는 계절 패턴을 보였다(그림 16). 공간적으로는 Weddell Sea의 경우 11월부터 점차 높은 농도를 보이기 시작하다가 2월부터 농도가 낮아지기 시작했으며, South Shetland islands 부근에서는 12월부터 농도가 높아지기 시작했는데, 2월경에 가장 높은 농도 분포를 보였다(그림 17). 월별 엽록소 농도에 대한 표준편차는 평균 엽록소 농도의 분포와 비슷한 패턴을 보였는데, 특히 농도가 높았던 1월의 경우 Shetland islands 부근에서 편차가 가장 컸으며, 12월에는 Weddell Sea에서 높은 편차를 보였다(그림 18).

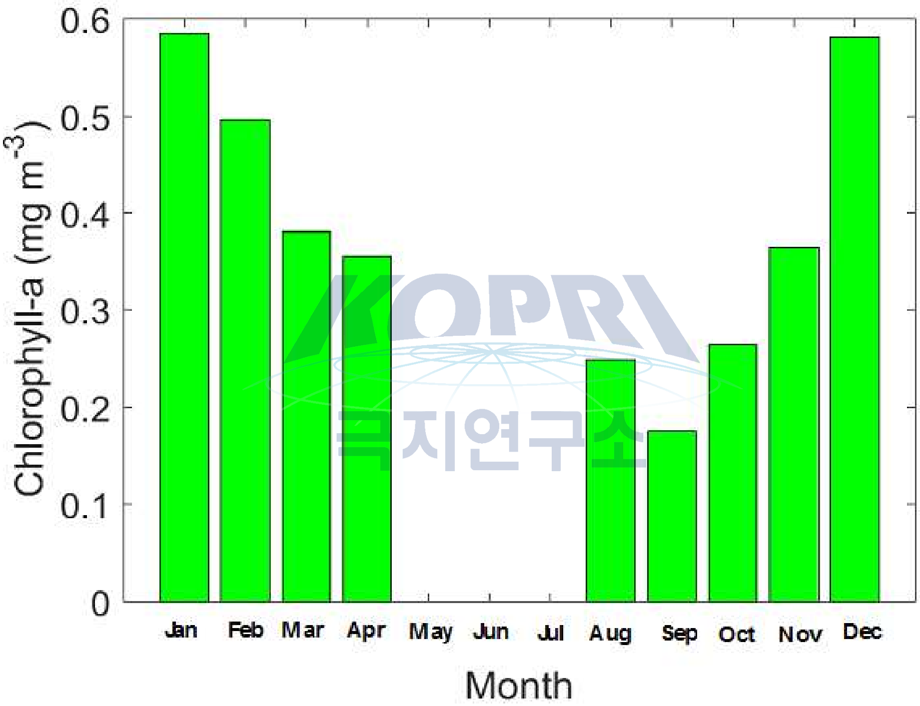


그림 16 월별 평균 엽록소-a 농도.

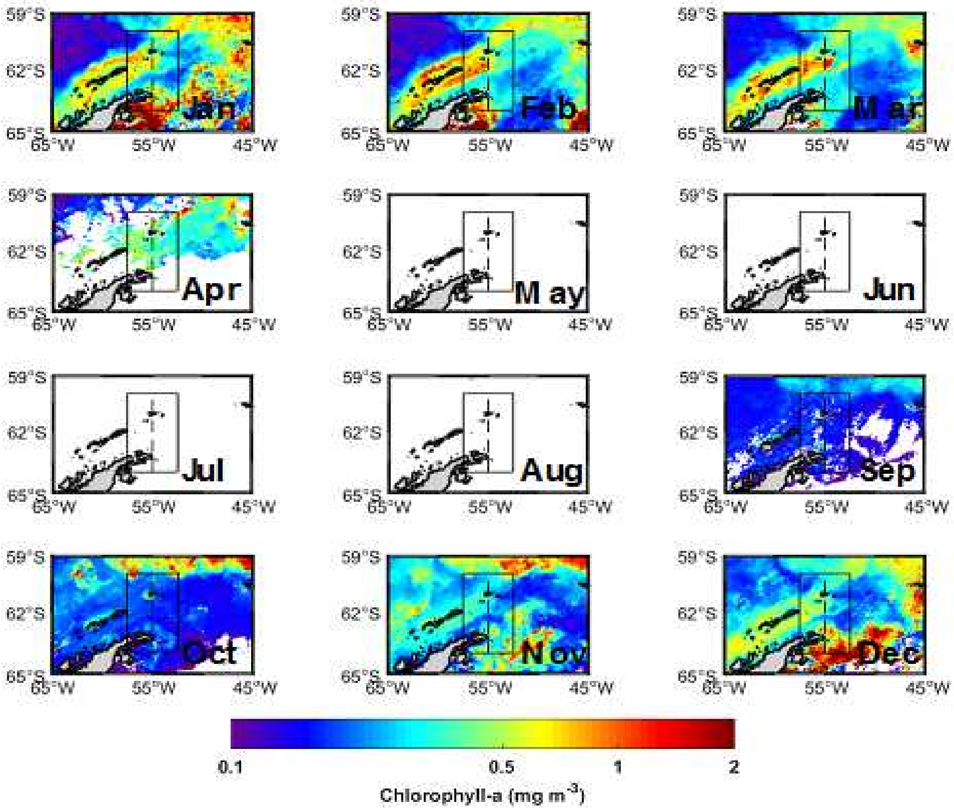


그림 17 월별 평균 엽록소-a 농도 분포(2002-2016년).

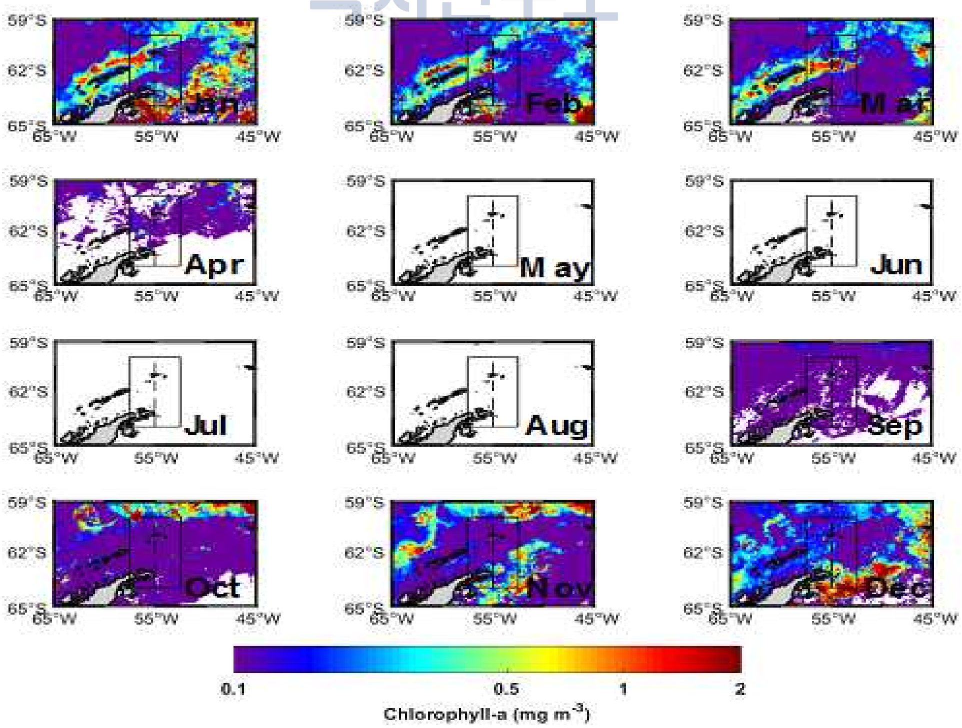


그림 18 월별 엽록소-a 농도의 표준편차(2002-2016년).

3.2.3.7 월별 엽록소 농도 분포

위 엽록소 농도 평균에 사용한 2002년부터 2016년까지의 월별 엽록소 농도를 <부록 1>에 나타내었다.

3.2.4 향후 진행 방향

1차 년도 연구를 통해 남극 반도 탄소 저감 후보 지역을 포함하는 Weddell-Scotia Sea에 대해 전반적인 해양 환경 특성의 시공간적인 변화를 파악할 수 있었으나 국지적 규모의 eddy의 특성을 파악하는 데는 한계가 있었다. 따라서 2차 년도에는 1 km의 공간해상도를 가지는 해색 위성 자료를 사용하여 남극 반도 부근의 탄소 저감 후보지역에 초점을 맞춰 최근 5년간 엽록소-a 농도 및 표층수온의 변화를 토대로 eddy의 발생 시기, 패턴, 크기, eddy의 안과 밖에서의 해양 환경 특성의 변화를 분석하고자 한다. 해색 위성자료는 2011년 10월 28일에 발사된 Suomi NPP (National Polar-orbiting Partnership)의 해양관측센서인 VIIRS의 Level-1a와 Level-2의 엽록소-a 농도와 표층수온 자료를 사용하여 분석할 예정이다. 고해상 해색위성 자료를 활용하기 위해 NASA에서 개발한 해색 위성자료 처리용 소프트웨어인 SeaDAS (SeaWiFS Data Analysis System)를 통해 처리할 것이며, VIIRS 해색자료를 2012.1.2 - 2016.12.31기간의 남극 반도 탄소 저감 후보 지역(60-64°S, 52.5-57.5°W)에 대해 일별 및 8일 합성자료로 생산하여 분석하고자 한다.

3.3 과거 Ocean Iron Fertilization 실험 리뷰

3.3.1 연구배경

▶ 산업혁명이후로 인간 활동은 대기 중의 CO_2를 ~280 ppm(산업혁명 이전)부터 ~400 ppm(현재) 까지 급속하게 증가시켰으며, 이러한 변화는 지구 온난화와 해양 산성화와 같은 기후변화현상을 야기하고 있다(IPCC, 2013). 전 세계적으로 지구온난화 문제 등의 이상 기후현상을 막기 위한 다양한 과학 기술적 방안들이 대두되고 있는데, 대표적으로 'ocean fertilization'과 'carbon dioxide capture & storage'등의 대기 중의 CO_2를 감축시키는 방법과 'artificial aerosol injection into the atmosphere'과 같은 태양에너지를 제어하는 방법이 있다. 이중에서도 경제적, 사회적, 과학적 측면에서 식물플랑크톤의 성장을 제한하는 철, 질소, 인등과 같은 영양염을 추가하여 해양생물펌프를 통해 대기 중의 CO_2를 감축시키는 'ocean fertilization'은 최근 가장 주목받고 있는 방안이다.

▶ 해양생물펌프는 표층에서 식물플랑크톤에 의해 광합성을 통해 생성된 유기물이 심층으로 빠르게 제거되는 기작을 말하며(그림 19a), 이 기작은 주로 질산염, 인산염, 규산염과 같은 'macro-nutrients'의 공급과 철과 같은 'micro-nutrient' 공급의 영향을 받는다(Volk and Hoffert, 1985; Martin and Fitzwater 1988). 특히 'High-Nutrient and Low-Chlorophyll (HNLC)' 지역인 아북극 태평양, 적도태평양 및 남극해 지역은 철의 공급이 제한된 지역으로 macro-nutrients가 풍부함에도 일차생산력이 상대적으로 낮게 나타나는 특징을 보여준다(그림 20). 과거 20,000년 전에 나타난 'Last Glacia Maximum(LGM)'은 대기 중 CO_2 농도(~180 ppm)가 산업혁명 이전 시기에 나타난 농도(~280 ppm)보다 훨씬 낮은 농도를 보였다(Broecker, 1982; Falkowski, 1997; Broecker and Henderson, 1998). Martin (Martin, 1990)은 LGM 시기동안의 낮은 CO_2 농도 메커니즘에 대해 일반적으로 자연적인 철 공급원으로 알려진 dust의 유입이 HNLC 지역(특히, 남극해)으로 증가됨에 따라 철 제한이 경감되어 생물펌프가 증가된 결과였을 것이라는 가설을 주장하였다(그림 19b). Martin의 가설이후 대기 중의 CO_2 농도를 감소시키기 위한 방향으로 인위적으로 철을 HNLC지역에 공급하여 해양의 생물펌프를 강화 시키는 'Ocean Iron Fertilization (OIF)'에 초점이 맞춰져 많은 연구가 진행되었는데(ACE, 2008), 현재까지 총 13번의 인위적인 OIF 실험과 2번의 자연적인 OIF 실험이 수행되었다.

▶ 본 과제에서는 남극해 남극반도/로스해역에서의 OIF 실험을 하기에 앞서 과거 진행되었던 OIF 실험들을 조사하고 각 실험의 목적과 결과를 살펴봄으로써 본 과제에서 최종적으로 수행하고자 계획하는 남극해 남극반도/로스해역에서의 OIF 실험에 대한 방향을 수립하고자 하였다.

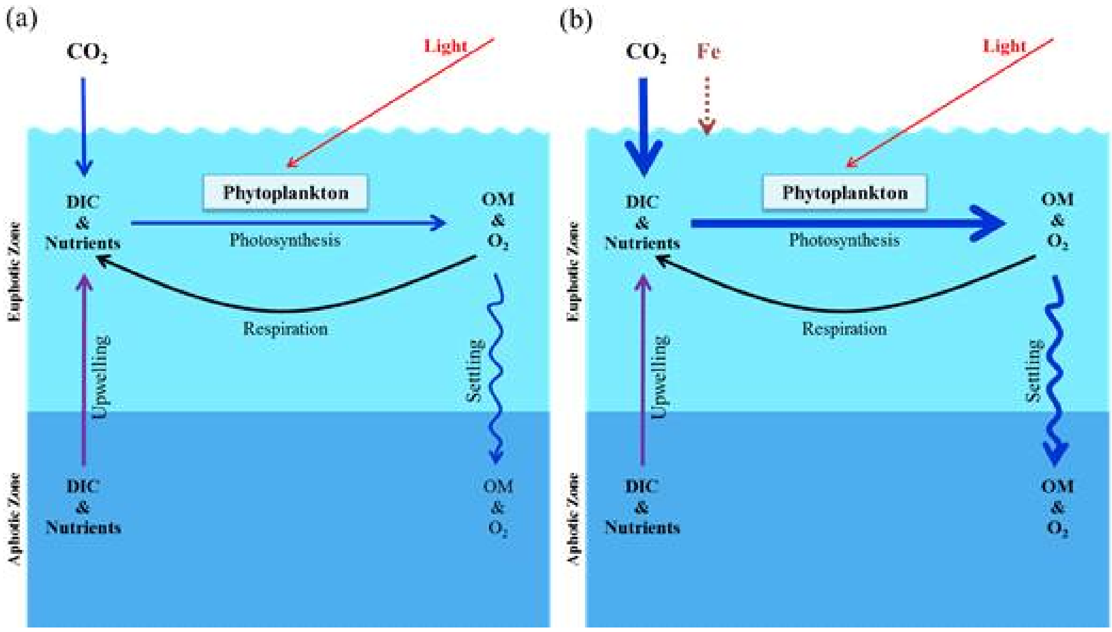


그림 19 철 가설을 나타내는 모식도 (modified from Martin (1990)). (a) 정상상태에서의 생물펌프 효일 펌프 효율과 (b) 철의 유입에 따른 생물펌프의 효율. DIC는 용존 무기 탄소(Dissolved Inorganic Carbon)를 나타내며, OM(Organic Matter)은 유기물질을 나타낸다(modified from Sarmiento and Gruber, 2006).

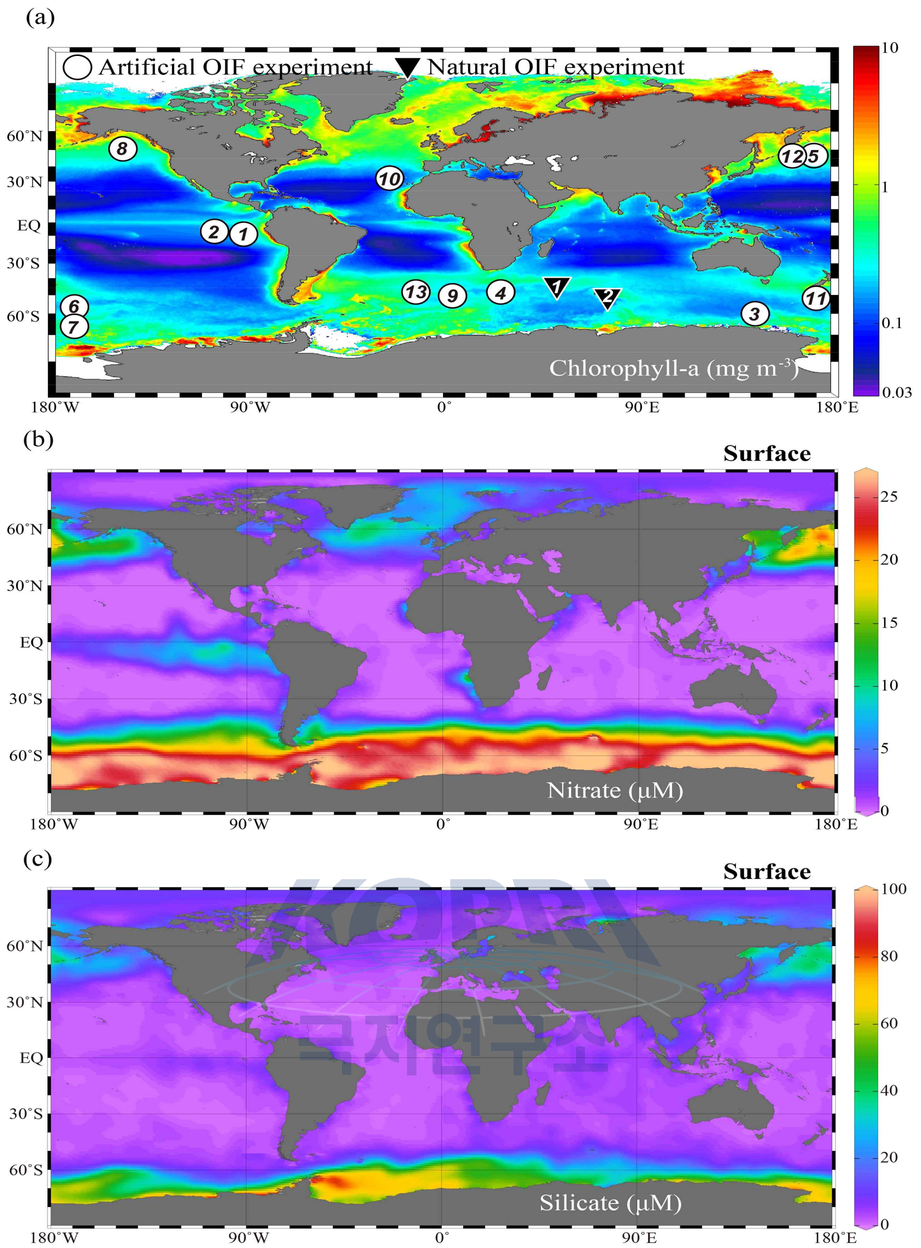


그림 20 전 지구적 연간 (a) 표층 엽록소-a 농도의 분포 (mg m^{-3}), (b) 표층 질산염 농도의 분포 (μM), (c) 표층 규산염 농도의 분포 (μM). 엽록소-a 농도 분포 자료는 MODIS Aqua 자료의 2002년 7월부터 2016년 2월까지의 합성자료이며 (http://oceancolor.gsfc.nasa.gov/cgi/l3), 질산염과 규산염 농도는 World Ocean Atlas 2013 (https://odv.awi.de/en/data/ocean/world_ocean_atlas_2013) 자료로 Ocean Data View program (https://odv.awi.de)을 사용하여 분포를 나타냄. 흰색 동그라미는 13개의 인위적인 철 주입 실험 지역들을 나타내며, 검은색 세모는 자연적인 철 주입 실험 지역들을 나타낸다. 마커 안의 숫자는 철 주입 실험의 순서를 나타낸다(표 3).

3.3.2 연구 결과 및 토의

▶ 과거 OIF 실험에 대한 요약

◆ Martin의 가설을 검증하기 위해 과거 총 2번의 자연적인 OIF 실험과 13번의 인위적인 OIF 실험은 아북극 태평양, 아열대 대서양, 적도태평양, 남극해에서 진행되었다(Blain et al., 2007; Pollard et al., 2009; Strong et al., 2009) (그림 20a, 표 3). 특히 본 년도에는 본 과제에서 목표로 하는 인위적인 OIF 실험에 대해 조사하였다. 인위적인 OIF 실험은 HNLC 지역(질산염 농도 >10 μM)인 아북극 태평양에서 3번, 적도태평양에서 2번, 남극해에서 7번에 걸쳐 진행되었으며, 'Low-Nutrient and Low-Chlorophyll (LNLC)' 지역(질산염 농도 <10 μM)인 아열대 대서양에서는 1번 수행되었다 (표 3). 시간에 따른 과거 OIF 실험을 순서대로 표 3에 나타냈으며, 각 OIF 실험이 수행된 해역을 그림 20a에 표시하였다.

◆ 과거 OIF 실험의 철 주입량 및 patch 크기
각 실험은 iron-sulfate ($FeSO_4 \cdot H_2O$)를 최소 총 350 kg (SEEDS-1)에서 최대 4000 kg (LOHAFEX)을 1-4번에 걸쳐 주입하였으며, 첫 번째 주입을 기준으로 철이 추가된 해역의 patch 크기는 25 km^2 (FeeP- 1840 kg) 부터 300 km^2 (LOHAFEX- 2000 kg)까지 다양하였다(Boyd et al., 2007; Martin et al., 2013) (표 3, 그림 21a). 철이 추가되기 전의 용존 철 농도는 0.2 nM 이하였는데, 철을 주입함에 따라 ~1.0-4.0 nM까지 증가되었다. 이 농도는 수일 내에 기존 농도로 감소되는 경향을 보였다(표 3, 그림 21b).

◆ 과거 OIF 실험의 patch 추적 방법
과거 OIF 실험들은 철이 추가된 patch를 추적하기 위해 생지화학적 방법 및 물리적 방법을 적용하였다. 먼저 생지화학적인 방법으로써 EIFEX 실험을 제외한 모든 실험에서 sulfur hexafluoride (SF_6)을 추적자로써 사용하였다. SF_6는 비교적 값이 저렴하고 무독성이며 생지화학적으로 비활성인 특징을 갖는데, 철과 함께 주입하여 gas chromatography를 사용하여 연속적으로 농도를 측정하였다(Law et al., 1998; Tsumune et al., 2005). 또한 Underway sampling system으로 생지화학적인 변수들을 측정하여 patch를 추적하였는데, 사용한 변수들은 photosynthetic quantum efficiency (Fv/Fm ratio), CO_2 partial pressure (pCO_2) 및 엽록소 농도였다(Gervais et al., 2002; Boyd et al., 2005; Tsuda et al., 2007; Harvey et al., 2010; Smetacek et al., 2012). 물리적 방법으로는 Array for Real-time Geostrophic Oceanography (ARGO) 와 Global Positioning System (GPS) sensors를 사용하여 patch의 시, 공간적인 이동을 추적할 수 있었다(Coale et al., 1998; Boyd and Law, 2001; Law et al., 2006; Martin et al., 2013).

◆ 각 실험이 진행된 해양 환경은 철을 주입하기 이전에 사전 조사를 통해 분석되었는데, 각 실험은 물리적으로 혼합층의 깊이가 10 m (SEEDS-1)에서 97.6 m (EIFEX)이며(그림 21c), 표층 수온이 -0.5 °C (SOFeX-S)부터 25.2 °C (IronEx-2)까지의 다양한 해양 환경에서 실험이 수행되었다(그림 21d). 생지화학적으로는 질산염 농도는 7.9 μM (SAGE)부터 26.3 μM (SOFeX-S)로 높은 농도를 보이고(그림 21e, 표 4), 엽록소 농도는 0.04 mg m^{-3}

(FeeP) 부터 0.9 mg m^{-3} (SEEDS-1) 까지로 상대적으로 낮은 농도의 특징을 보였다(그림 21h, 표 5). 특히 식물플랑크톤의 광합성 효율의 측정지표인 Fv/Fm 비율의 경우 철에 의한 제한이 적을수록 1에 가깝고, 철에 의한 제한이 심하게 일어날수록 0에 가까워지는데, 모든 실험 대상해역에서 0.3보다 낮은 값을 보였다(그림 21g, 표 3).

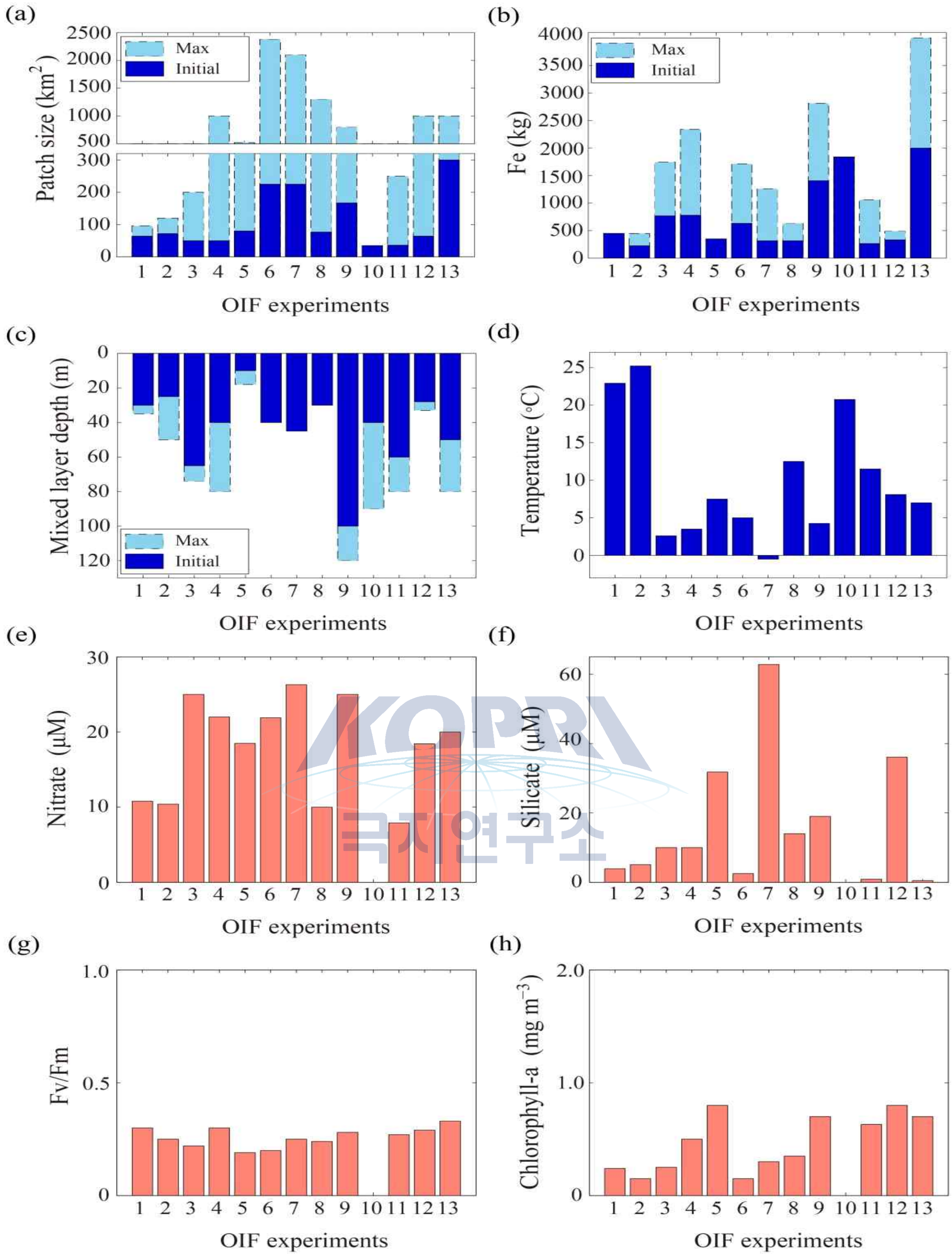


그림 21 (a) 각 실험의 첫 번째 철 주입에 의해 결정된 patch 크기(km^2) (파란색 막대그래프)와 철 실험 기간 동안의 최대 patch 크기(하늘색 막대그래프). (b) 각 실험의 첫 번째 철 주입 양(kg) (파란색 막대그래프)과 철 주입 총량(하늘색 막대그래프). (c) 혼합층의 최소(파란색막대그래프) 및 최대(하늘색 막대그래프) 깊이(m). 철 주입 이전 상태에서의 (d) 평균 표층 수온(°C), (e) 질산염 및 (f) 규산염 철 농도(μM), (g) Fv/Fm 비, (h) 엽록소-a 농도(mg m^{-3}). 각 실험의 숫자는 각 실험의 순서를 나타냄(표 3).

표 3 과거 철 주입(Ocean Iron Fertilization; OIF) 실험들의 요약; 시기, 위치, 연구선, 철 주입량, 정상상태에서의 철농도, 철 주입후의 철농도, 추적자, 첫 번째 철 주입에 의해 결정된 patch 크기, 실험기간 및 연구해역의 특징.

	Experiment	Time	Location	Research Vessel	Fe (kg) (day)	Initial Fe (nM)	After Fe (nM)	Tracer	Patch size (km^2)	Period (days)	Region
1	IronEx-1	Oct 1993	5° S, 90° W Equatorial Pacific	RV *Columbus Iselin*	①450 (0)	0.06	3.6	SF_6	64	10	HNLC
2	IronEx-2	May 1995	3.5° S, 104° W Equatorial Pacific	RV *Melville*	①225 (0) ②112 (3) ③112 (7)	0.02	2 1 1	SF_6	72	17	HNLC
3	SOIREE	Feb 1999	61° S 141° E Southern Ocean- Australasian-Pacific sector	RV *Astrolab*	①768 (0) ②312 (3) ③312 (5) ④353 (7)	0.08	3.8 2.6 2.6 2.5	SF_6	50	13	HNLC
4	EisenEx	Nov 2000	48° S, 21° E Southern Ocean- Atlantic Sector	RV *Polarstern*	①780 (0) ②780 (7) ③780 (16)	0.06	2	SF_6	50	23	HNLC
5	SEEDS-1	Jul-Aug 2001	48.5° N, 165° E North Pacific- Western subarctic gyre	RV *Kaiyo-Maru*	①350 (0)	0.05	2.9	SF_6	80	13	HNLC
6	SOFeX-N	Jan-Feb 2002	56.23° S, 172° W Southern Ocean- Atlantic sector	RV *Revelle* RV *Melville*	①631 (0) ②631 (5) ③450 (30)		1.2	SF_6	225	40	HNLCLSi
7	SOFeX-S	Jan-Feb 2002	66.45° S, 171.8° W	RV *Revelle* RV *Melville* RV *Polarstar*	①315 (0) ②315 (4) ③315 (7) ④315 (11)		0.7	SF_6	225	28	HNLC
8	SERIES	Jul-Aug 2002	50.14° N, 144.75° W North Pacific- Eastern subarctic Pacific	RV *John P. Tully* RV *El Puma* RV *Kaiyo Maru*	①315 (0) ②315 (6)	<0.1	2 0.6	SF_6	77	25	HNLC

계속

	Experiment	Time	Location	Research Vessel	Fe (kg) (day)	Initial Fe (nM)	After Fe (nM)	Tracer	Patch size (km^2)	Period (days)	Region
9	EIFEX	Feb-Mar 2004	50° S, 2° E Southern Ocean- Atlantic sector	RV *Polarstern*	①1406 (0) ②1406 (13)	0.2	1.5 0.34		167	39	HNLC
10	FeeP	Apr-May 2004	27.5° N 22.5° W North Atlantic- Sub-tropical north-East Atlantic	RV *Charles Darwin* RV *Poseidon*	①1840 (0)	0.2	3.0	SF_6	25	21	LNLC
11	SAGE	Mar-Apr 2004	46.7° S 172.5° E Southern Ocean- Southeast of New Zealand	RV *Tangaroa*	①265 (0) ②265 (6) ③265 (9) ④265 (12)	0.09	3.03 1.59 0.55 1.01	SF_6	36	15	HNLCLSi
12	SEEDS-2	Jul-Aug 2004	48° N, 166° E North Pacific- Western subarctic gyre	RV *Hakuho-Maru* RV *Kilo-Moana*	①332 (0) ②159 (6)	0.17	1.38	SF_6	64	26	HNLC
13	LOHAFEX	Jan-Mar 2009	48° S, 15° W Southern Ocean- Atlantic sector	RV *Polarstern*	①2000 (0) ②2000 (21)		2.0	SF_6	300	40	HNLCLSi
1	CROZEX*	Nov 2004- Jan 2005	44° S, 50° E Southern Ocean-South of Sub-Antarctic Front	RV *Discovery*		0.039	0.55				HNLC
2	KEOPS*	Jan-Feb 2005	50° S, 73° E Southern Ocean- South of Polar Front	RV *Marion Dufresne*							HNLC

* Natural OIF experiments

표 4 각 OIF 실험 해역에서의 화학변수 초기값과 OIF 실험이후의 값. *ΔDIC는 DIC농도의 변화를 나타냄(i.e., [DIC]post-fertilization – [DIC]pre-fertilization).

	Experiment	Initial NO_3 (μM)	After NO_3 (μM)	Initial PO_4 (μM)	After PO_4 (μM)	Initial Si (μM)	After Si (μM)	Initial pCO_2 (ppm)	After pCO_2 (ppm)	*ΔDIC (μM)
1	IronEx-1	10.8 ±0.4	10.1	0.92 ±0.02	0.9	3.9	3.88	471	458	-6
2	IronEx-2	10.4 ±0.3	6.4	0.8 ±0.03	0.55	5.1	1.1	538	465	-27
3	SOIREE	25.0	22.0	1.5		10.0	7.0	350	312-318	-(18-15)
4	EisenEx	22.0	21.0	1.6	1.5	10.0	10.0	360	340-342	-(15-12)
5	SEEDS-1	18.5	2.7		0.44	31.8	5.0	390	260	-58
6	SOFeX-N	21.9	20.5	1.40	1.31	2.5	1.4	367	341	-13
7	SOFeX-S	26.3	22.8	1.87	1.66	62.8	58.8	365	329	-21
8	SERIES	10-12	3.0	>1.0	<0.5	14.0-16.0	<2.0	350	265	-36
9	EIFEX	25.0	23.5	1.8	1.5	19.0	8.0	360	330	-13.5
10	FeeP	<0.01		0.01						<-1
11	SAGE	7.9-10.3	11.8	0.62-0.85		0.83-0.97		330	338	25
12	SEEDS-2	18.42	12.7			36.1		370	364	
13	LOHAFEX	20.0	17.5	1.3	1.1	0.5-1.4				

표 5 각 OIF 실험 해역에서의 생물변수 초기 값과 OIF 실험이후의 (최대)값. *PP (mg C m^{-2} d^{-1})는 표층 PP (mg C m^{-3} d^{-1})과 혼합층 깊이를 곱함으로 추정됨.

	Experiment	Initial Fv/Fm	Maximum Fv/Fm	Initial Chlorophyll (mg m^{-3})	Maximum Chlorophyll (mg m^{-3})	Initial PP (mg C m^{-2} d^{-1})	Maximum PP (mg C m^{-2} d^{-1})
1	IronEx-1	0.30	0.60	0.24	0.65	300-450*	805-1330*
2	IronEx-2	0.25	0.50	0.15-0.20	4.0	630	2430
3	SOIREE	0.22	0.65	0.25	2.0	120	1300
4	EisenEx	0.30	0.56	0.50	2.5	130-220	790
5	SEEDS-1	0.19	0.31	0.80-0.90	21.8	420	1670
6	SOFeX-N	0.20	0.50	0.15	2.6	144	1500
7	SOFeX-S	0.25	0.65	0.30	3.8	216	972
8	SERIES	0.24	0.55	0.35	5.0	300	2000
9	EIFEX	0.28	0.60	0.70	3.16	750	1500
10	FeeP			0.04	0.07		
11	SAGE	0.27	0.61	0.63	1.33	540	900
12	SEEDS-2	0.29	0.40	0.80	2.48	390	1000
13	LOHAFEX	0.33	0.4-0.5	0.5	1.25	960	1560

◆ 과거 OIF 실험의 목적 및 결과

① IronEx-1 (First OIF experiment): Martin의 가설을 테스트하기 위해 진행된 첫 번째 실험으로 적도 태평양에서 1993년 10월에 약 10일동의 기간 동안 수행되었다(Martin et al., 1994; Coale et al., 1998). 본 실험이 수행된 지역은 갈라파고스 섬의 남쪽부근으로 따뜻한 수온 및 높은 광도로 식물플랑크톤의 성장이 빠르게 일어나며, 접근이 용이한 특징을 가지고 있다. 또한 타 연구지역에 비해 상대적으로 연구가 많이 되어있어 물리적, 생지화학적인 특징에 대한 자료가 충분히 축적되었고, 자연적인 철 공급이 일어나는 해역으로 인위적인 철 실험 이전에 철의 공급에 따른 해양 생산성의 변화에 대한 조사를 가능하게 한 해역이다(Martin and Chisolm, 1992; Martin et al., 1994). 그러나, 본 실험에서는 결과적으로 철을 주입함에 따른 생지화학적인 반응이 예상된 것만큼 크게 일어나지 않았으며, 다른 실험들에 비해 생지화학적 인자에 대한 변화량이 가장 적었다(그림 22, 표 4, 표 5). 철 주입에 대한 반응이 작은 이유에 대해 수층의 불안정한 구조로 인한 철의 체류시간의 감소, 동물플랑크톤에 의한 포식의 증가, 카드뮴이나 망간과 같은 철 이외의 다른 micro-nutrient의 제한 가능성 등의 여러 요인들이 가설로 대두되었다(Cullen, 1995).

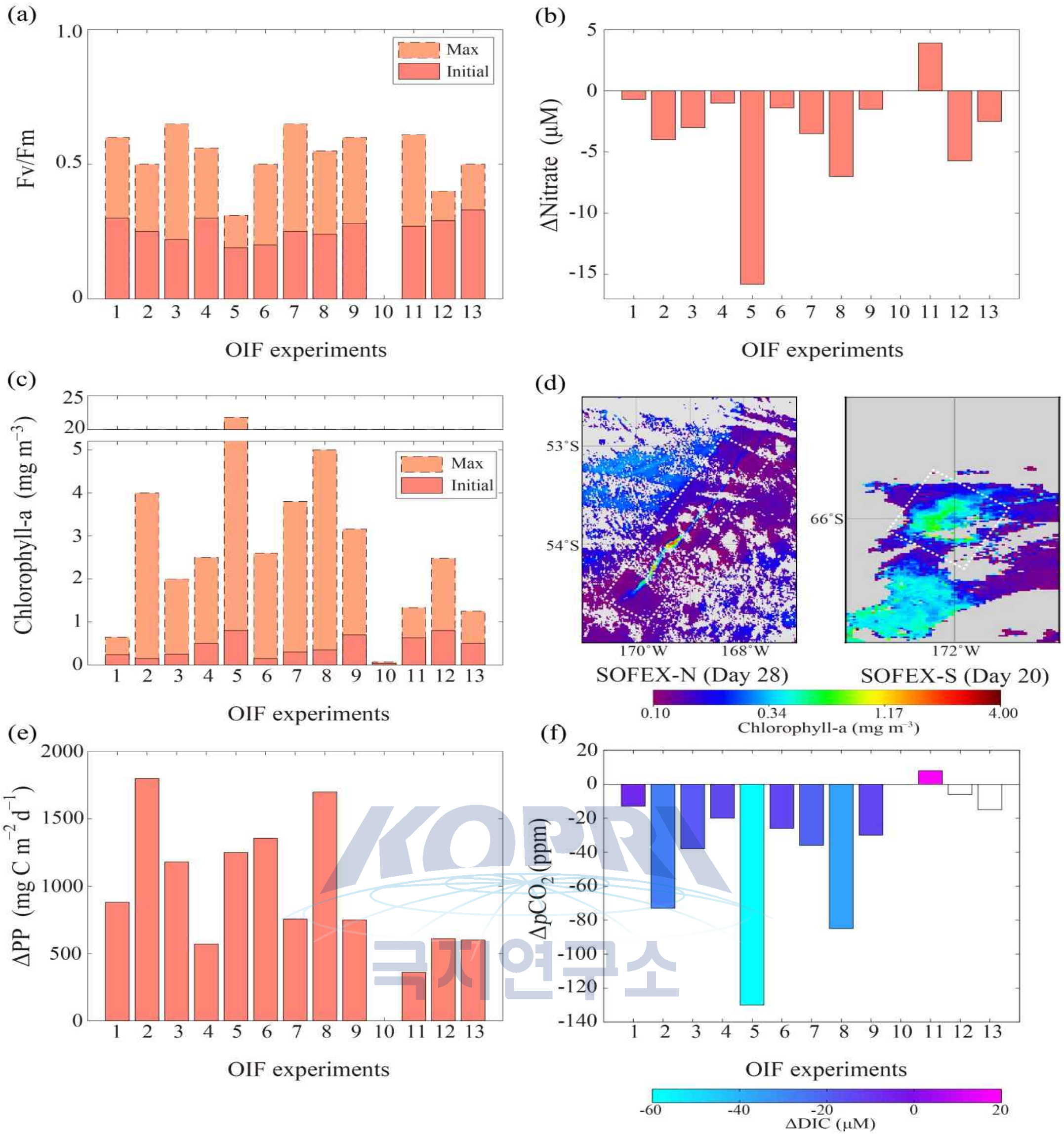


그림 22. (a) OIF 실험기간동안의 Fv/Fm 비의 초기값(주황색 막대그래프) 및 최대값(옅은 최대값 (옅은 주황색 막대그래프). (b) 질산염 농도 변화(ΔNitrate = $[NO_3^-]$post-fertilization – $[NO_3^-]$pre-fertilization; μM). (c) 엽록소 농도(mg m^{-3})의 초기값(주황색 막대그래프) 및 최대값(옅은 주황색). (d) SOFeX-N 실험기간 동안 철 주입이후 28일째 되는 날의 엽록소 농도의 공간 분포 및 SOFeX-S 실험기간 동안 철 주입 이후 20일째 되는 날의 엽록소 농도의 공간분포. 하얀색 점선 박스는 식물플랑크톤의 번성을 나타냄. (e) 일차생산 변화(ΔPP = [PP]post-fertilization – [PP]pre-fertilization; mg C m^{-2} d^{-1}). (f) pCO_2의 변화(ΔpCO_2 = $[pCO_2]$post-fertilization – $[pCO_2]$pre-fertilization; ppm). Color bar는 DIC의 변화값을 의미함(ΔDIC = [DIC]post-fertilization – [DIC]pre-fertilization; μM). OIF 실험 number 1 (IronEx-1)의 PP값(mg C m^{-2} d^{-1})은 표층 PP값(mg C m^{-3} d^{-1})에 혼합층의 깊이를 곱해 추정하였으며, x축의 numbers는 각 실험의 순서를 의미함(표 3).

② IronEx-2 (Second OIF experiment): IronEx-1의 예상치 못한 반응의 결과를 조사하기 위해 같은 해역에서 IronEx-1의 조사기간 대비 더 긴 기간 동안 1995년 5월에 총 17일 동안 OIF 실험이 진행되었다. 결과적으로 IronEx-2 실험은 인위적인 철 주입에 따른 식물플랑크톤의 번성이 강하게 발생하는 결과를 처음으로 밝힐 수 있게 하였다(Coale et al., 1996; Bidigare et al., 1999). 인위적인 철 주입에 대한 반응은 식물플랑크톤의 번성, 즉 엽록소 농도의 증가 및 일차생산성의 증가 외에도 질산염의 감소 및 pCO_2, 무기탄소의 감소, Fv/Fm의 증가의 결과를 보였으며, 식물플랑크톤의 군집구조가 nano-plankton으로부터 생물펌프에 있어 중요한 종으로 micro-plankton인 규조류가 우점하는 군집구조로 변화되었다(Coale et al., 1996; Landry et al., 2000).

③ SOIREE (Southern Ocean iron release experiment): IronEx-2 실험이 적도 태평양에서의 OIF 실험의 성공적인 결과를 보여줌에 따라 다른 HNLC 지역에서의 철 실험에 대한 기대를 가지게 하였다. 남극해는 HNLC 지역 중 가장 넓은 해역으로 특히 중층수와 심층수 형성에 있어 중요하며, 철 주입에 따른 탄소 고정에 큰 잠재력을 가지고 있는 해역으로 주목받아왔다(Martin, 1990; Sarmiento and Orr, 1991; Cooper et al., 1996; Marshall and Speer, 2012). 이에 따라 1999년 2월에는 남극해 태평양 섹터에서 첫 번째 남극해 철 주입 실험이 약 13일 기간 동안 수행되었다. 결과적으로, 본 실험을 통해 남극해에서도 인위적인 철 주입에 의해 식물플랑크톤의 번성이 강하게 발생하는 현상을 확인할 수 있었다(그림 22, 표 4, 표 5).

④ EisenEx ('Eisen'is iron in German): SOIREE 실험의 성공 이후 남극해에서 대서양 섹터에서 2000년 11월에 총 23일의 기간 동안 OIF 실험이 수행되었다. EisenEx 실험은 처음으로 eddy가 형성된 환경에서 실험이 진행되었으나, 실험기간동안 폭풍이 발생하여 물리적으로 혼합이 강하게 일어나 주입된 철의 농도가 급격하게 감소되었다(Smetacek, 2001).

⑤ SEEDS-1 (Subarctic Pacific iron Experiment for Ecosystem Dynamics Study-1): 적도 태평양 및 남극해외의 HNLC 지역 중 또 다른 해역인 아북극 태평양은 dust의 공급에 의해 자연적인 OIF에 의해 영향을 받는 해역으로 dust의 공급은 경도별 편차가 크게 나타난다(Duce and Tindale, 1991). OIF에 따른 경도별 식물플랑크톤의 반응에 대한 결과를 살펴보기 위하여, 2001년 8월에 먼저 서쪽의 아북극해 환류지역에서 총 13일의 기간 동안 실험이 진행되었다. 인위적인 OIF에 따른 식물플랑크톤의 반응은 다른 실험에 비해 가장 크게 발생했는데, Fv/Fm ratio는 철 주입 후 0.65까지 증가되었고, 질산염은 최대 15.8 μM가 고정되었으며, 엽록소 농도는 22 mg m^{-3}로 가장 높게 증가하였다(Tsuda et al., 2003) (그림 22, 표 4, 표 5).

⑥ SOFeX-N (Southern Ocean iron experiment-north) & ⑦ SOFeX-S (Southern Ocean iron experiment-south): SOFeX-N 와 SOFeX-S는 export production에 있어 중요한 식물플랑크톤인 규조류가 세포골격을 구성하는데 필요한 영양염인 규산염 농도의 차이에 따른 OIF에 대한 식물플랑크톤의 반응을 조사하고자 남극해에서 수행된 실험으로 SOFeX-N는 규산염 농도가 5 μM 이하로 낮은 해역이며, SOFeX-S는 규산염 농도가 60 μM 이상으로 높은 농도의 해역이다(Coale et al., 2004; Hiscock and Millero, 2005) (그림 21). OIF 실험에 따른 생지

화학적 반응은 규산염 농도가 높은 SOFeX-S가 SOFeX-N에 비해 크게 일어났으며, 식물플랑크톤 군집구조의 경우 SOFeX-S는 규조류가 우점하였으나 SOFeX-N에서는 다른 종에 비해 규조류의 우점도가 낮은 구조를 보이는 차이가 나타났다(그림 22) (Coale et al., 2004). 철 주입에 따른 식물플랑크톤의 반응은 해색 위성 자료인 MODIS 엽록소 농도 자료를 통해서도 확인 할 수 있었다(그림 22d).

⑧ SERIES (Subarctic Ecosystem Response to Iron Enrichment Study): SERIES는 북동태평양 지역에서 2002년 7-8월에 약 25일의 기간 동안 조사되었으며, OIF 실험에 따른 식물플랑크톤의 번성의 시작부터 종료되는 시기까지의 반응을 분석하는 것을 목표로 연구가 진행되었다. 이에 따라 앞선 타 실험들과 달리 연구기간동안 철 주입 이후 식물플랑크톤이 증가되기 시작하는 것부터 peak에 도달한 후 감소되는 패턴을 확인할 수 있었다(Boyd et al., 2004, 2005).

⑨ EIFEX (Southern Ocean European Iron Fertilization Experiment): EIFEX 이전 실험들은 대부분 표층에서의 식물플랑크톤의 번성에 초점이 맞춰져 실험이 진행됨에 따라 OIF가 생물펌프에 있어 표층에서 번성한 식물플랑크톤이 심해로 빠르게 이동되는 export production을 증가시키는지에 대해서는 명확한 결과를 얻을 수 없었다(그림 23b) (Boyd et al., 2007). 따라서 EIFEX에서는 export production을 증가시키고자 남극해 cyclonic eddy에서 약 39일 기간 동안 실험이 진행되었다(Smetacek et al., 2012). 결과적으로 철을 주입하고 약 30일 이후부터 철이 뿌려진 patch에서 입자성 유기탄소의 증가된 값을 확인할 수 있었다(그림 23a).

⑩ FeeP (in situ $PO_4^{3-}$and Fe^{2+} addition experiment): LNLC 지역에서 인산염과 철을 동시에 추가함으로써 생산성의 반응을 확인한 실험으로 21일의 기간 동안 실험이 진행되었다. 결과적으로 타 실험에 비해 식물플랑크톤의 성장이 적게 일어났다(Rees et al., 2007).

⑪ SAGE (Surface Ocean Lower Atmosphere Study (SOLAS) Air - Sea Gas Exchange): SOFeX-N와 같이 규산염 농도가 낮은 해역에서 실험이 진행되었으며, CO_2외에도 dimethylsulfide, CO, N_2O, N_2, 및 O_2와 같은 기체 발생을 측정하고자 아남극해 지역에서 약 15일의 기간 동안 조사되었다. 그러나 본 실험의 경우 타 실험들과 달리 오히려 질산염이나 pCO_2의 농도가 철 주입이후 증가되는 경향을 보였는데, 이는 물리적으로 patch 밖의 해수와 강하게 혼합되어 발생하였다(Harvey et al., 2010; Law et al., 2011) (그림 22, 표 4).

⑫ SEEDS-2 (Subarctic Pacific iron Experiment for Ecosystem Dynamics Study-2): SEEDS-1 실험과 같은 해역 및 시기에 진행되었다. 그러나 본 실험의 결과는 SEEDS-1 실험과 비교해 상대적으로 OIF에 따른 식물플랑크톤의 반응이 적게 나타났는데, 이러한 차이는 copepod가 SEEDS-1에 비해 5배나 많이 존재함에 따른 포식의 효과 때문인 것으로 보인다(Tsuda et al., 2007).

⑬ LOHAFEX (Indian and German Atlantic sector iron fertilization experiment; 'Loha' is iron in Hindi): EIFEX 실험과 같은 위도이나 상대적으로 규산염이 낮은 해역에서 수행된 실험으로 본 실험은 표층에서의 식물플랑크톤의 번성과 export production외에도 고정된 탄소가 박테리아나 zooplankton에 의해 다시 CO_2로 전환되어 대기 중으로 방출되는 것을 조사하는 것을 목표로 과거 실험들 중 가장 긴 실험 기간인 40일 기간 동안 실험이 진행되었다(Smetacek and Naqvi, 2010; Martin et al., 2013). EIFEX와 같이 cyclonic eddy에 철이 주입되어 실험이 수행되었으나, 본 실험에서는 export production의 증가가 나타나지 않았다.

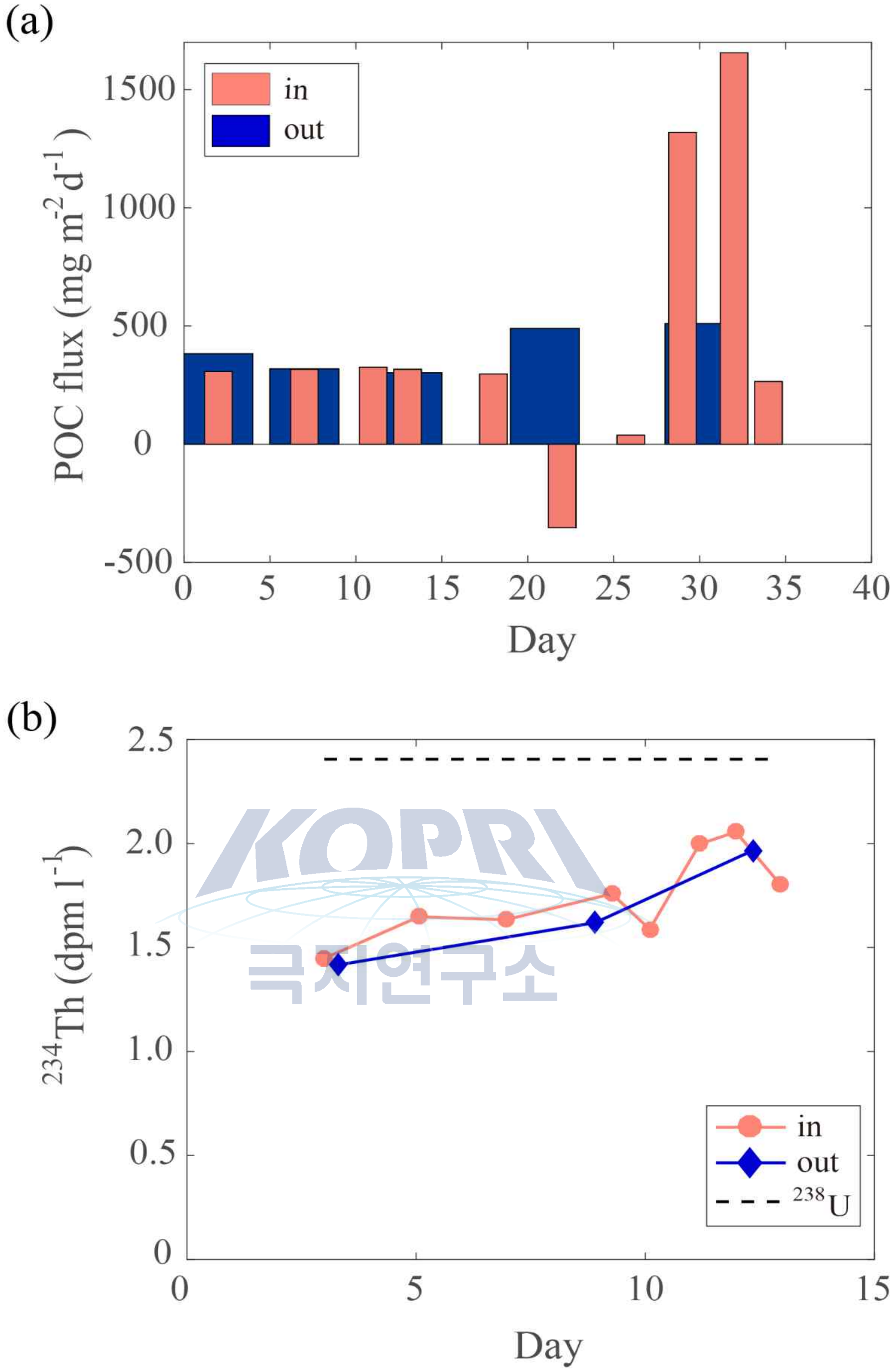


그림 23 (a) EIFEX 실험동안 ^{234}Th으로부터 추정된 상층 100 m 내의 patch 안(분홍색 막대그래프)과 patch 밖(파란색 막대그래프)에서의 입자성 유기탄소(particulate organic carbon; POC)의 시계열 fluxes 그래프(mg m^{-2} d^{-1}) (modified from Smetacek et al., 2012). (b) SOIREE 실험동안 patch 안(분홍색 동그라미 실선 그래프)과 patch 밖(파란색 다이아몬드 실선 그래프)에서 수직적으로 적분된(0-100 m) ^{234}Th (dpm l^{-1}) 및 238U (dpm l^{-1}; 검은색 점선)의 시계열 그래프(modified from Nodder et al., 2001).

▶ 과거 OIF 실험 결과를 토대로 향후 진행될 OIF 실험의 방향을 정리해보면, 철을 어떻게-어디서-언제 뿌릴지 정리하는 것이 중요한 요인인 것으로 판단된다.

◆ 어떻게: 먼저 어떻게 철을 해역에 주입하고 추적하는지에 대한 문제는 산성화된 iron(II) sulfate를 사용하여 철을 해역에 주입하고 철이 주입된 patch를 추적하기 위해 GPS와 ARGO equipped drifting buoys, SF6, Fv/Fm ratio, pCO_2, 및 chlorophyll fluorescence 등의 물리적-생지화학적 기술 및 변수 등을 적용하는 것이 필요해 보인다.

◆ 어디서: 어디에 철을 뿌려야 하는지에 대한 문제는 기존 연구결과를 통해 eddy에서 수행된 EIFEX 실험이 유일하게 export production의 증가를 관측할 수 있었다(Smetacek et al., 2012). OIF 실험은 철이 뿌려진 patch를 철 뿌려지지 않은 주변 해양 환경으로부터 고립하여 유지시키는 것이 중요하다. 해양의 eddy는 물리적으로 회전하는 수층구조를 만들어 자연적으로 주변 환경과의 고립된 환경을 조정한다. 따라서 eddy에서의 OIF 실험은 명확하게 철 주입에 따른 export production의 반응을 확인할 수 있게 할 것이다.

◆ 언제: 식물플랑크톤의 성장은 영양염 뿐만 아니라 빛에 의해서도 제한되기 때문에 언제 실험을 시작하는지 또한 OIF 실험에 있어 중요한 결정요인이 될 수 있다. 그러나 과거 남극해에서 수행된 철 실험의 경우 봄부터 늦은 여름까지 실험 진행 되었는데, 본 시기동안의 식물플랑크톤의 성장은 빛에 대한 제한보다 오히려 철의 공급에 의해 강하게 조절되는 것으로 나타났다. 따라서 봄부터 늦은 여름 안에 실험이 진행 될 경우 빛에 대한 영향은 상대적으로 철에 대한 영향보다 적을 것으로 판단된다. 또한 얼마나 오랜 시간 동안 실험이 진행될 지에 대한 부분은 과거 철 실험의 경우 조사기간이 식물플랑크톤의 번성이 시작될 때부터 끝나는 시기까지의 충분한 기간을 커버하지 못할 경우 철을 주입함에 따른 식물플랑크톤의 반응을 충분히 확인하기가 어렵다. 또한 export production의 반응이 관측되었던 EIFEX 실험의 경우 약 30일 이후부터 export production에 대한 증가가 나타나기 시작하는 미루어봤을 때 약 40일 이상의 충분한 조사기간이 필요한 것으로 판단된다.

◆ 최근 OIF 실험에 대한 런던협약/의정서가 개정되어 추후 OIF 실험의 경우 런던협약/의정서에서 권장하는 프로토콜에 따라 OIF 실험에 대한 절차를 따르고 실험에 대한 모니터링 및 사전 점검, 사후점검이 필수적이다(Resolution LP.4 (8), 2013).

제 4장 연구개발목표 달성도 및 대외기여도

4.1 연구개발 목표

연구개발 목표	남극해 철 비옥화 실험에 대한 환경진단 구축

세부 연구개발 목표	세부 연구개발 내용 및 범위
N_2O 측정 시스템 구축	• GC를 기반한 N_2O 측정 시스템 구축
남극해 철 실험의 최적 시기 및 해역 선정	• 인공위성 자료를 활용한 탄소 저감 후보지 해양 특성 분석

4.2 연구개발 목표 달성도

연구개발 목표	달성도 (%)									
	10	20	30	40	50	60	70	80	90	100
N_2O 측정 시스템 구축	━	━	━	━	━	━				
남극해 철 비옥화 실험의 최적 시기 및 해역 선정	━	━	━	━	━	━	━	━	━	━

- GC를 기반으로 Purge and trap 방법의 N_2O 측정 시스템을 구축하여 테스트까지 진행 하는 것을 목표로 하였으나, 장비 구축 관련 물품 항목 구입의 지연으로 인해 시스템 구축이 진행되지 못하였다. 하지만 연구 목적에 부합하고 최적화된 분석 시스템을 구축하기 위한 조사 및 보완이 이루어진 상태이므로 추후 장비가 구축이 되면 정확성 및 신뢰성이 높은 해양의 N_2O 자료가 구축되어 해양환경에서의 N_2O 분포에 대한 이해를 넓힐 수 있을 것이고 기후변화 연구에 중요한 기초자료로 활용 될 것으로 기대된다.
- 본 년도 사업에서는 저해상도 인공위성 자료를 활용하여 규조류 연니층이 발달되어 있는 남극반도 주변 해역의 식물플랑크톤의 번성 및 표층 수온의 계절별, 지역별 특성을 확인할 수 있었으며, 본 위성자료는 추후 남극해 탄소 저감 후보지 선정을 위한 자료로 사용될 수 있을 것으로 예상된다.
- 과거 철 시비 실험에 대한 리뷰 논문을 작성함으로 과거 이뤄졌던 철 시비 실험들의 특성과 장, 단점을 파악할 수 있었으며 향후 철 실험을 위한 중요한 환경 변수 및 실험 설계 요인들을 제시함으로 본 자료는 향후 남극해 철 시비 실험 중요한 기초 자료로 사용할 수 있을 것으로 예상된다.

제 5 장 연구개발결과의 활용계획

- 남극해 철 비옥화 실험 전후에 따른 환경변화(N_2O 발생)를 예측하고 인과관계를 규명할 수 있는 기초 자료 확보 및 제공
- N_2O 기체 분석 시스템 구축을 통한 원천 기술 확보
- 남극해 이외의 국내 영해에서 기술 적용 가능성을 검토 할 수 있는 파일롯 스터디 활용
- 기존에 수행되지 않은 선행연구를 통한 국내 해양 연구 발전에 기여
- 시스템 구축 후 보다 향상된 시스템을 위한 지속적인 시스템 개발 연구 필요
- 추후 고해상도 해색 위성자료를 활용하여 eddy의 발생지역을 찾고 남극해 철 실험을 위한 최적의 시기 및 해역을 선정을 위한 연구 필요

제 6 장 연구개발과정에서 수집한 해외과학기술정보

- NOAA ESRL Global Monitoring Division

미국 NOAA의 Earth System Reaserch Laboratory에서 GC-ECD detector를 활용한 전 지구적 N_2O 분석 시스템.

(https://www.esrl.noaa.gov/gmd/hats/insitu/cats/conc.php?site=mlo&gas=n2o)

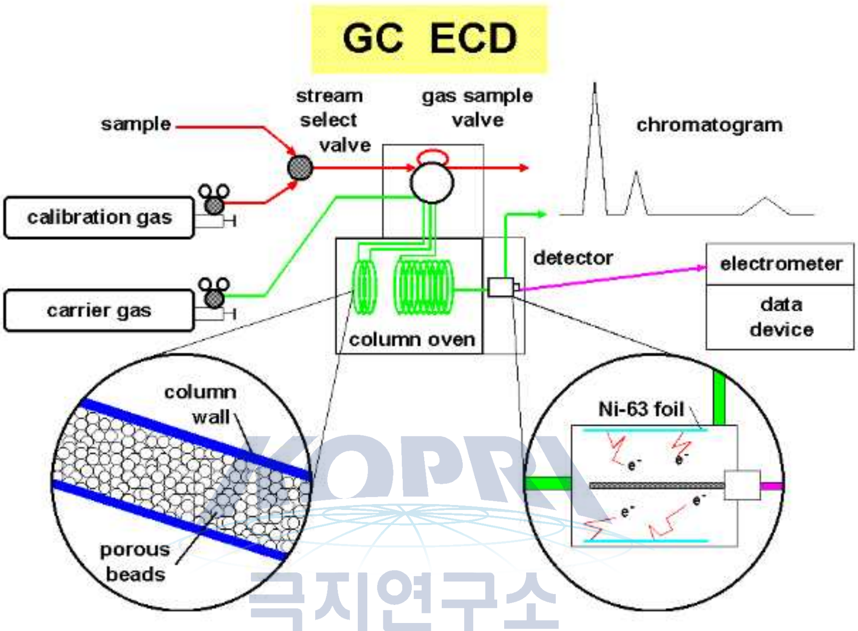


그림 24 NOAA ESRL에서 사용하는 N_2O 분석 시스템 모식도.

• Lightweight Airborn Chromatograph Experiment(LACE)

미국 콜로라도 대학의 Climate Monitoring and Diagnostics Laboratory (CMDL)에서 purge and trap 방법을 기반으로 한 N_2O 측정 시스템.

(https://cloud1.arc.nasa.gov/solve/balloon/lace.html)

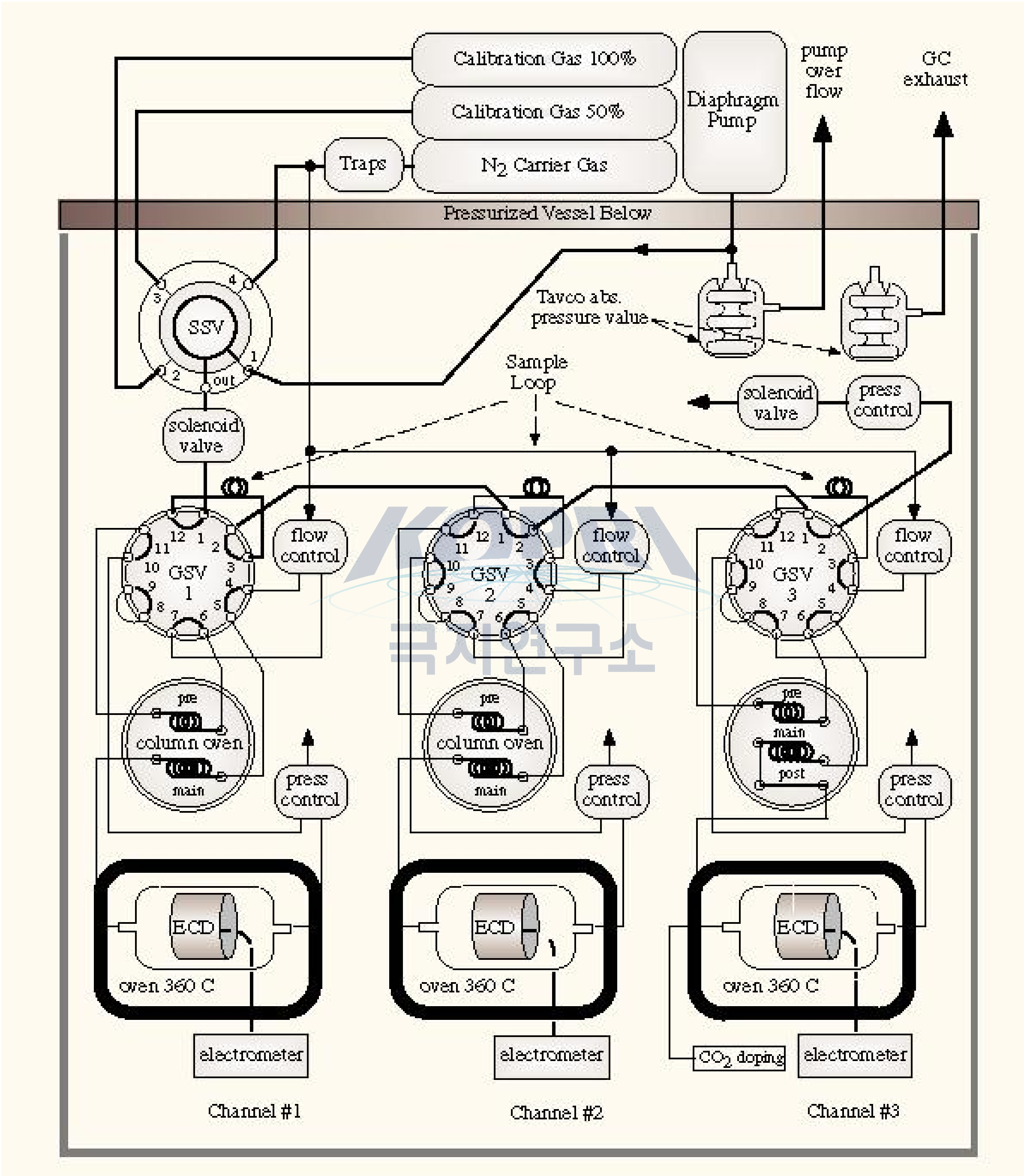


그림 25 미국 LACE에서 사용하는 N_2O 분석 시스템 모식도.

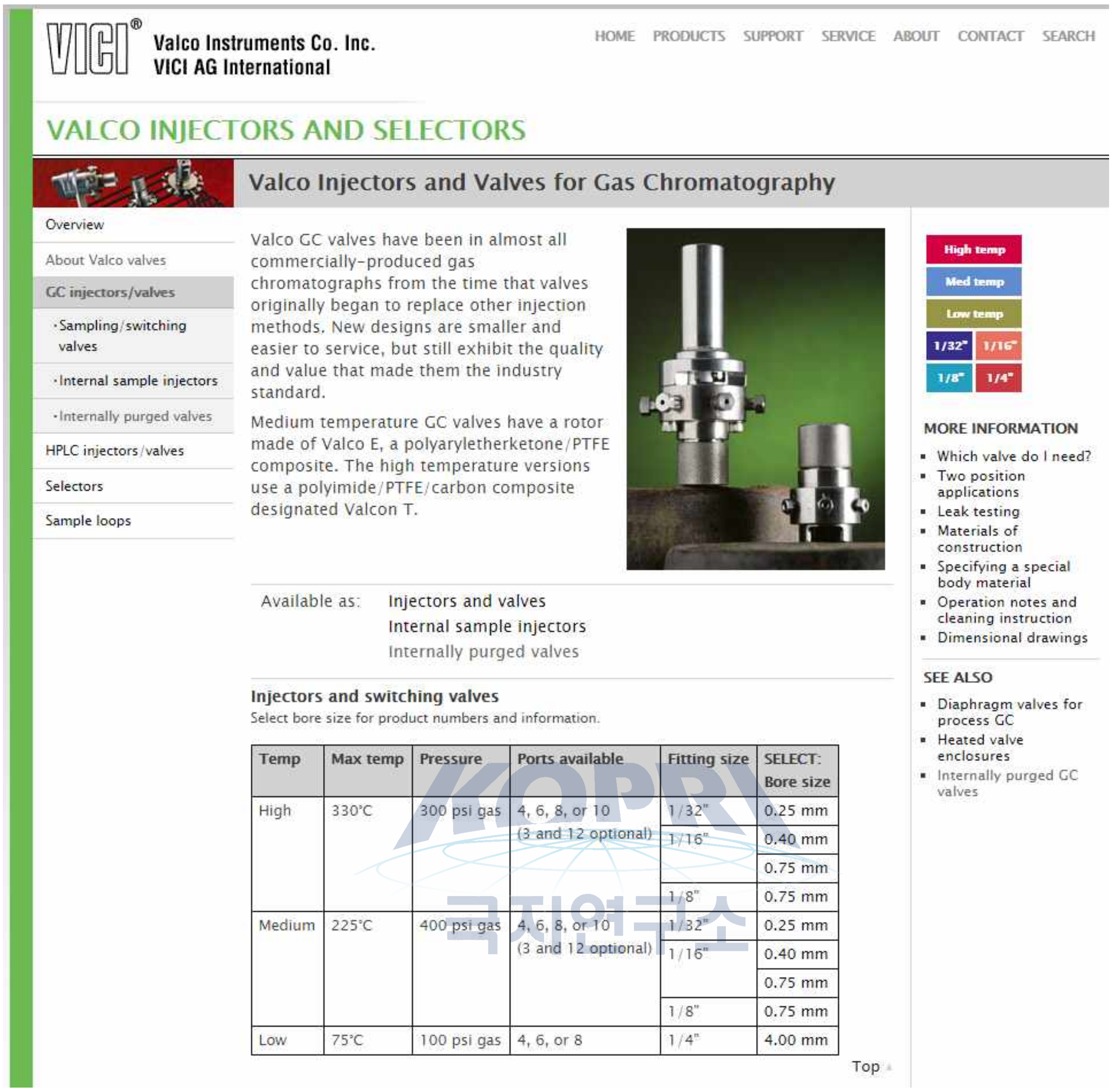
• N_2O 분석 시스템 구축을 위한 Swagelok, VICI® 제품 조사

N_2O 분석 전처리 장치에 필요한 주요 장비들(Valve, line, ferrule, loop 등등)을 제작하고 있다.

Swagelok: https://www.swagelok.com/en

VICI®: http://www.vici.com/vval/vval_gc.php

그림 26 N_2O 분석 전처리 시스템에 필요한 장비를 제작 및 판매하는 Swagelok 회사의 홈페이지.



Valco Instruments Co. Inc.
VICI AG International

HOME PRODUCTS SUPPORT SERVICE ABOUT CONTACT SEARCH

VALCO INJECTORS AND SELECTORS

Valco Injectors and Valves for Gas Chromatography

Overview
About Valco valves
GC injectors/valves
·Sampling/switching valves
·Internal sample injectors
·Internally purged valves
HPLC injectors/valves
Selectors
Sample loops

Valco GC valves have been in almost all commercially-produced gas chromatographs from the time that valves originally began to replace other injection methods. New designs are smaller and easier to service, but still exhibit the quality and value that made them the industry standard.

Medium temperature GC valves have a rotor made of Valco E, a polyaryletherketone/PTFE composite. The high temperature versions use a polyimide/PTFE/carbon composite designated Valcon T.

Available as: Injectors and valves
Internal sample injectors
Internally purged valves

Injectors and switching valves
Select bore size for product numbers and information.

Temp	Max temp	Pressure	Ports available	Fitting size	SELECT: Bore size
High	330°C	300 psi gas	4, 6, 8, or 10 (3 and 12 optional)	1/32"	0.25 mm
				1/16"	0.40 mm
					0.75 mm
				1/8"	0.75 mm
Medium	225°C	400 psi gas	4, 6, 8, or 10 (3 and 12 optional)	1/32"	0.25 mm
				1/16"	0.40 mm
					0.75 mm
				1/8"	0.75 mm
Low	75°C	100 psi gas	4, 6, or 8	1/4"	4.00 mm

Top

High temp
Med temp
Low temp
1/32" 1/16"
1/8" 1/4"

MORE INFORMATION
- Which valve do I need?
- Two position applications
- Leak testing
- Materials of construction
- Specifying a special body material
- Operation notes and cleaning instruction
- Dimensional drawings

SEE ALSO
- Diaphragm valves for process GC
- Heated valve enclosures
- Internally purged GC valves

그림 27 N_2O 분석 전처리 시스템에 필요한 장비를 제작 및 판매하는 VICI® 회사의 홈페이지.

• NASA 인공위성 자료

미국 NASA에서 제공하는 인공위성 해색 자료를 이용하여 남극해 철 실험 후보지에 대한 환경조사를 진행하였다.

https://oceancolor.gsfc.nasa.gov/cgi/l3

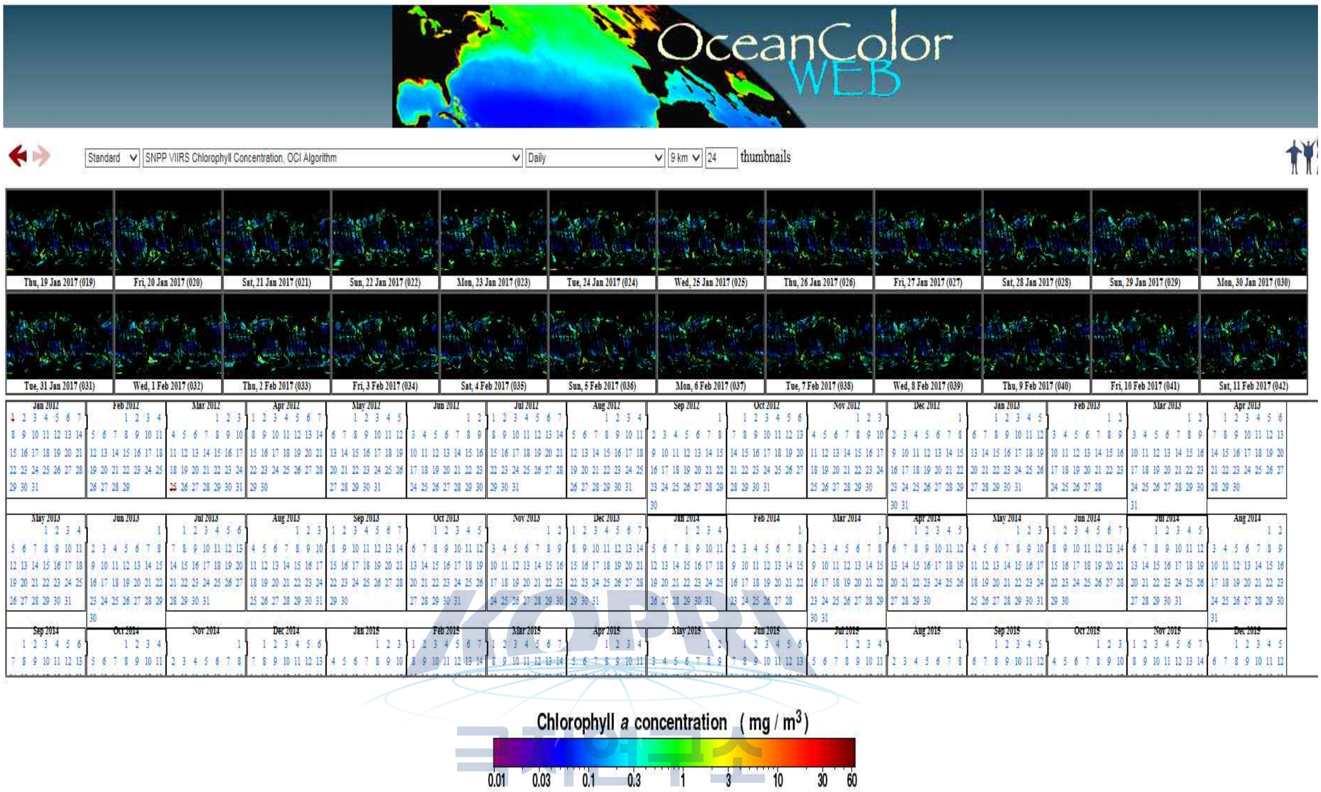


그림 28 NASA 인공위성 자료를 제공하는 홈페이지.

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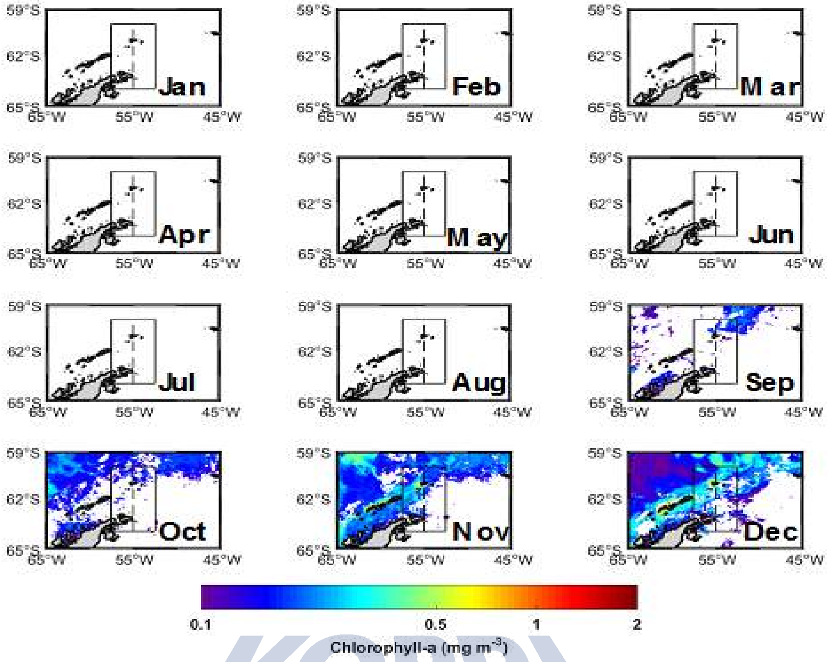
부록

1. 월별 엽록소- a 농도 분포



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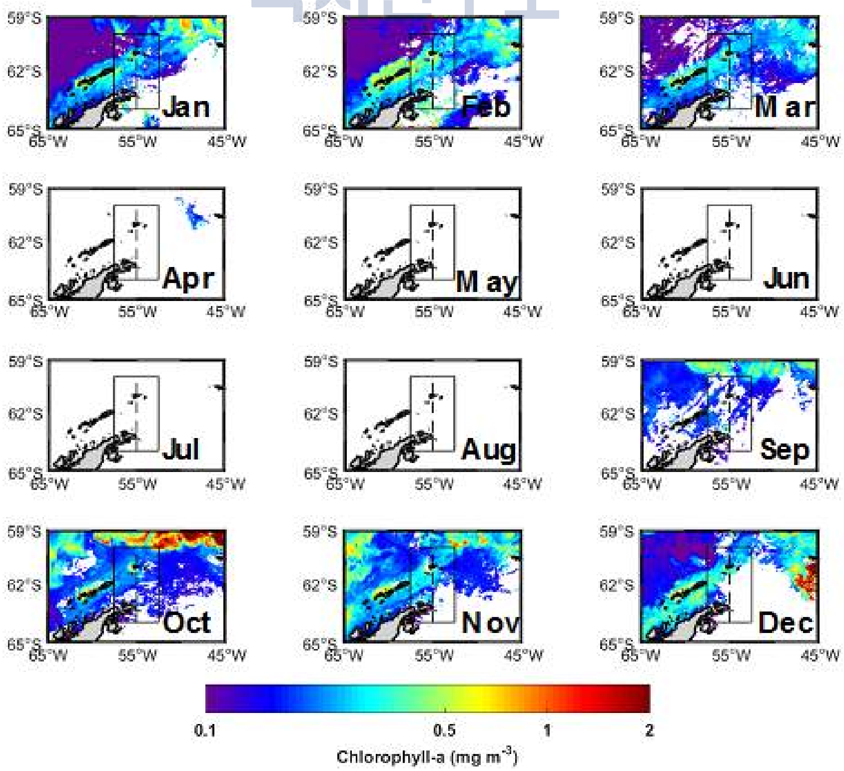

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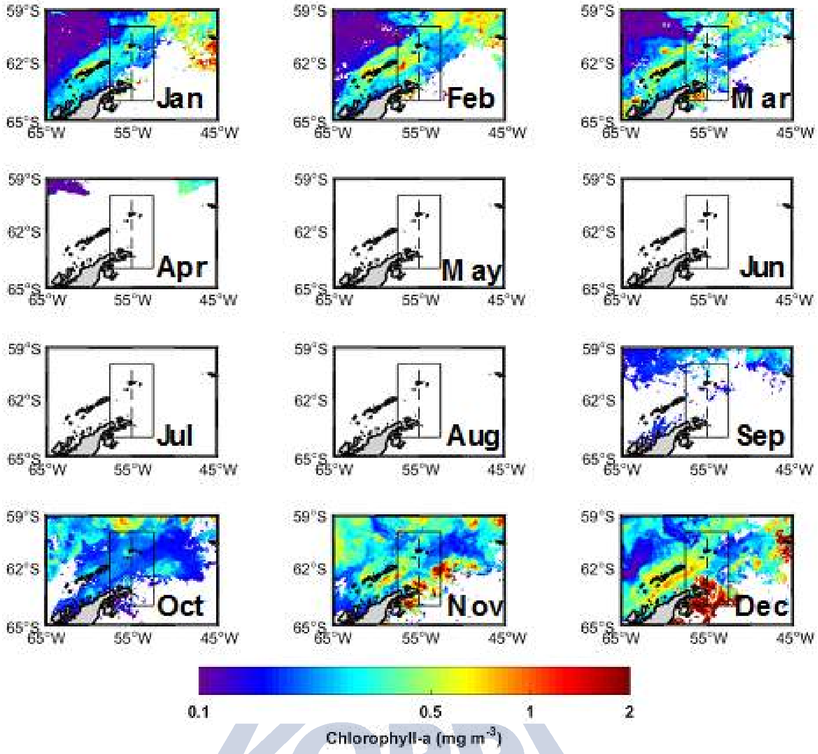

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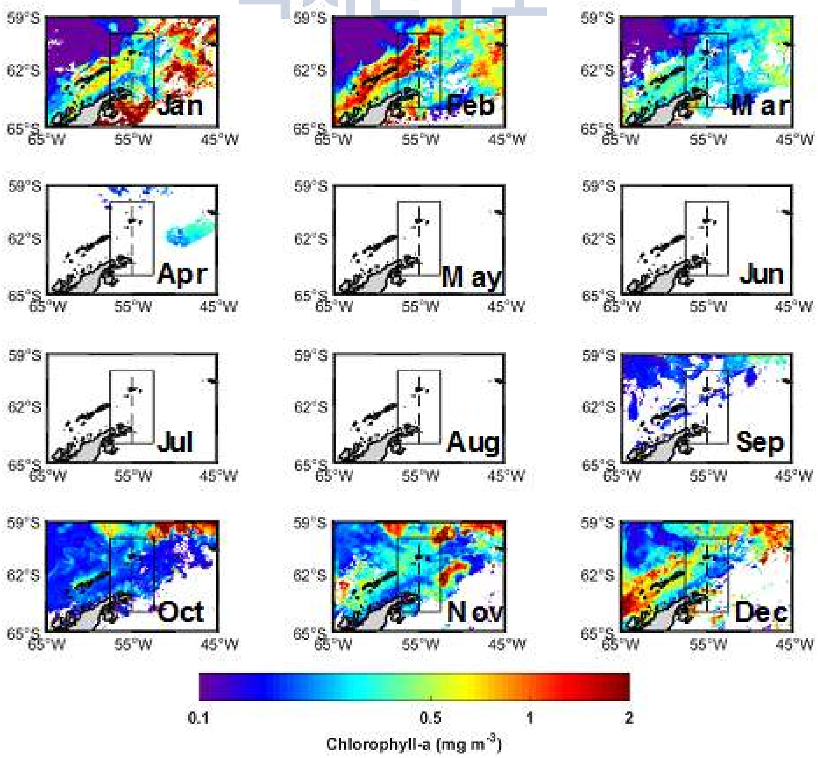

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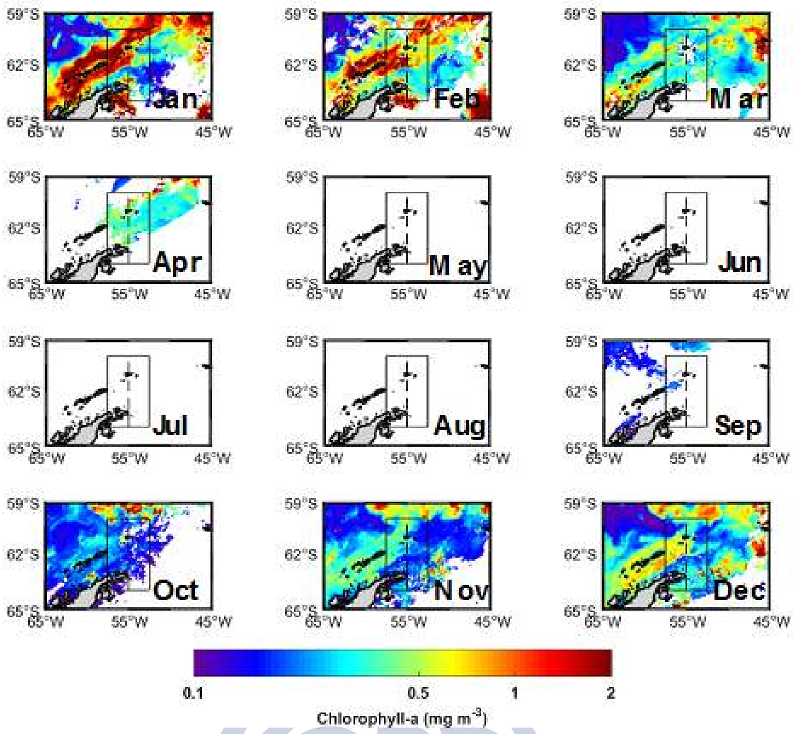

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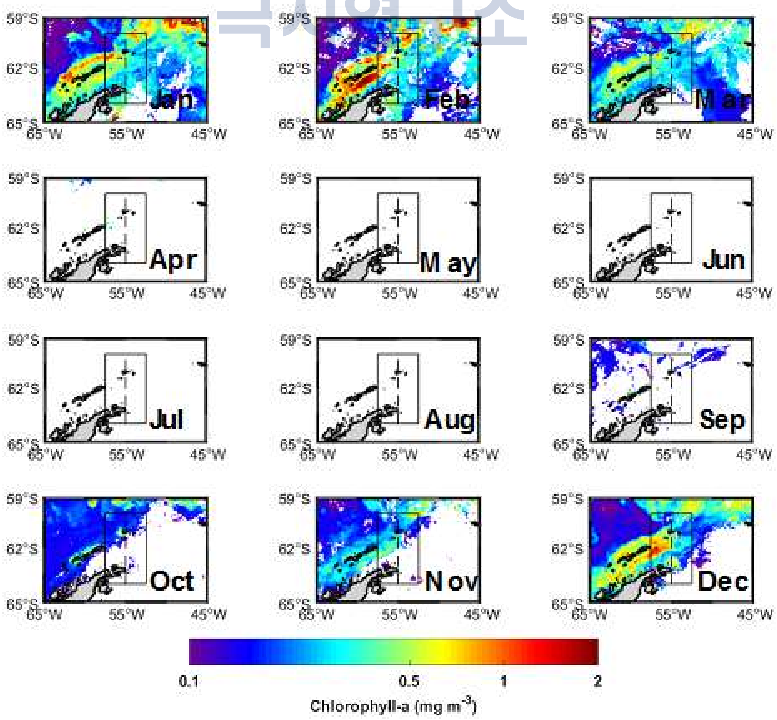

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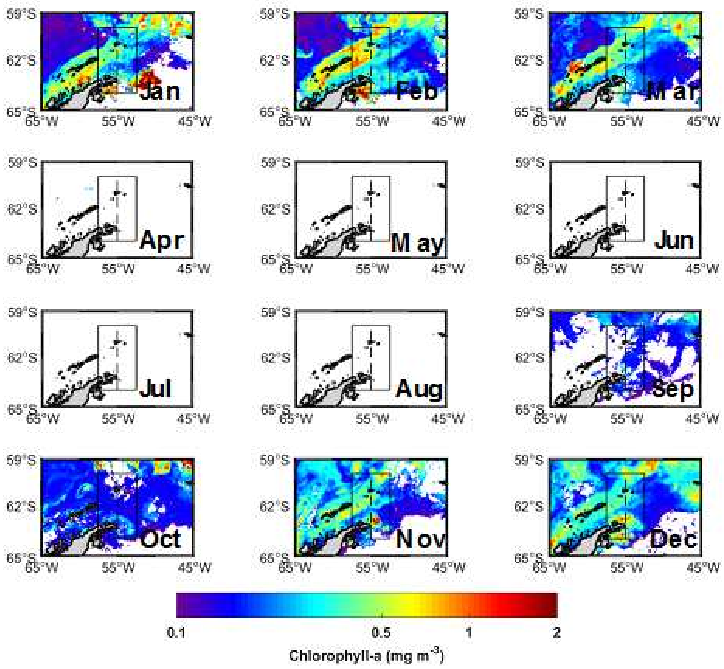

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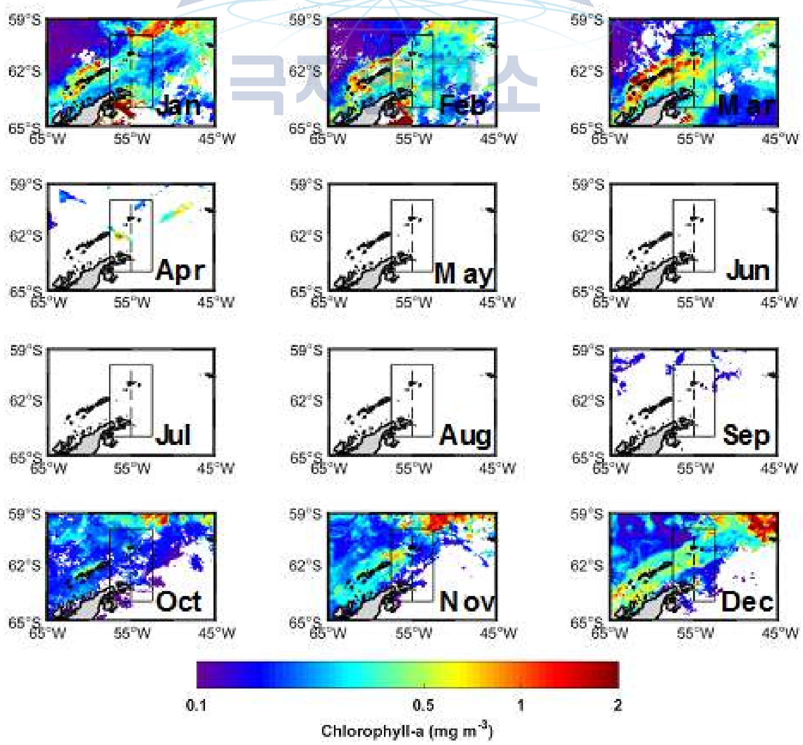

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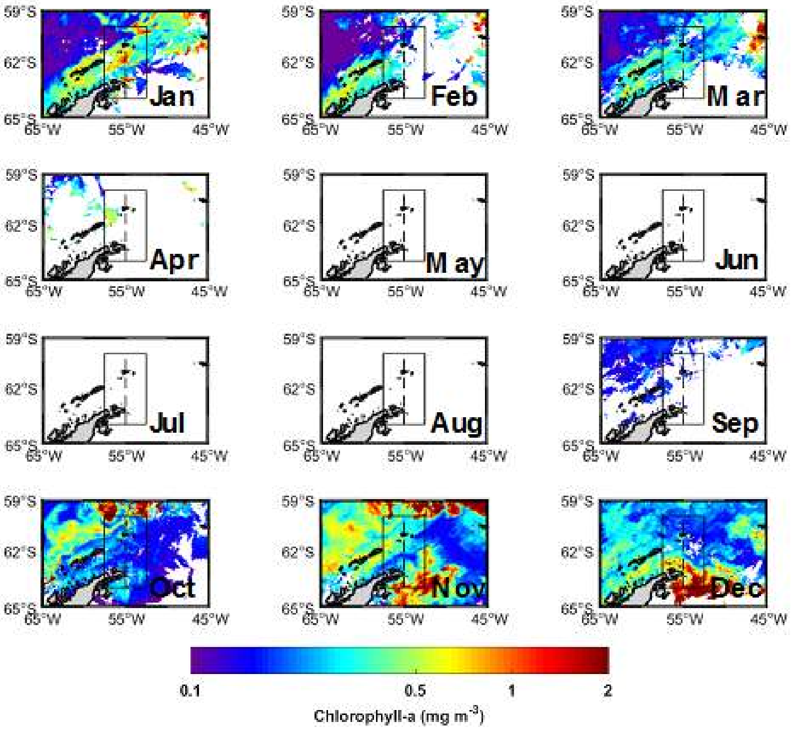

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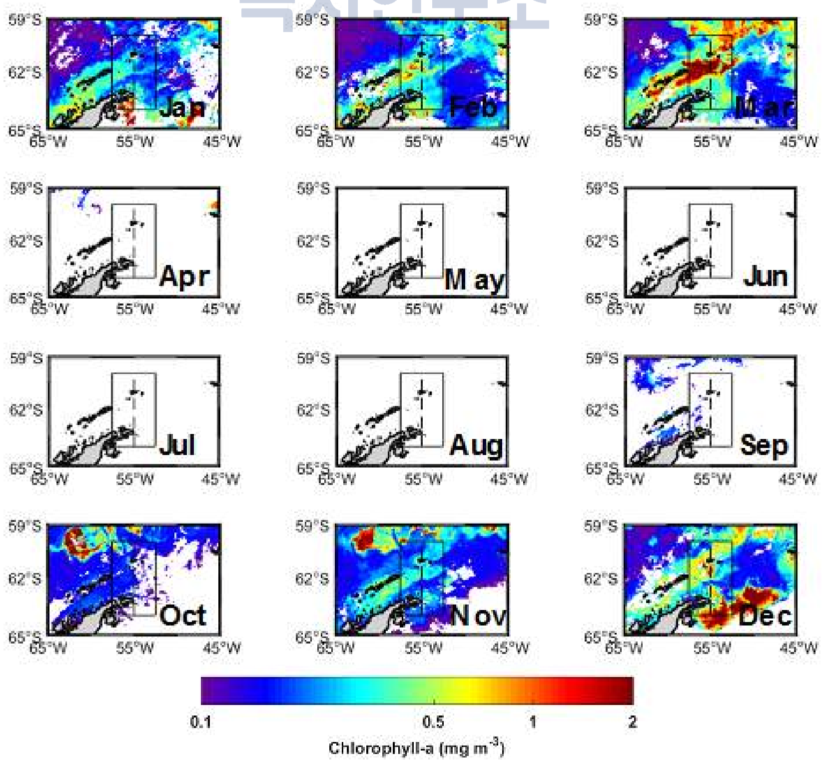

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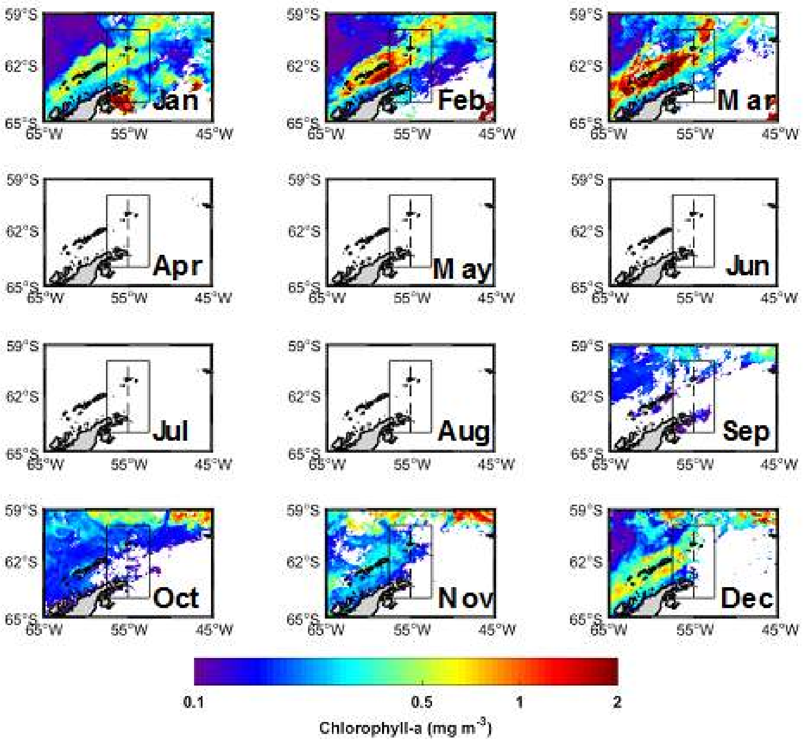

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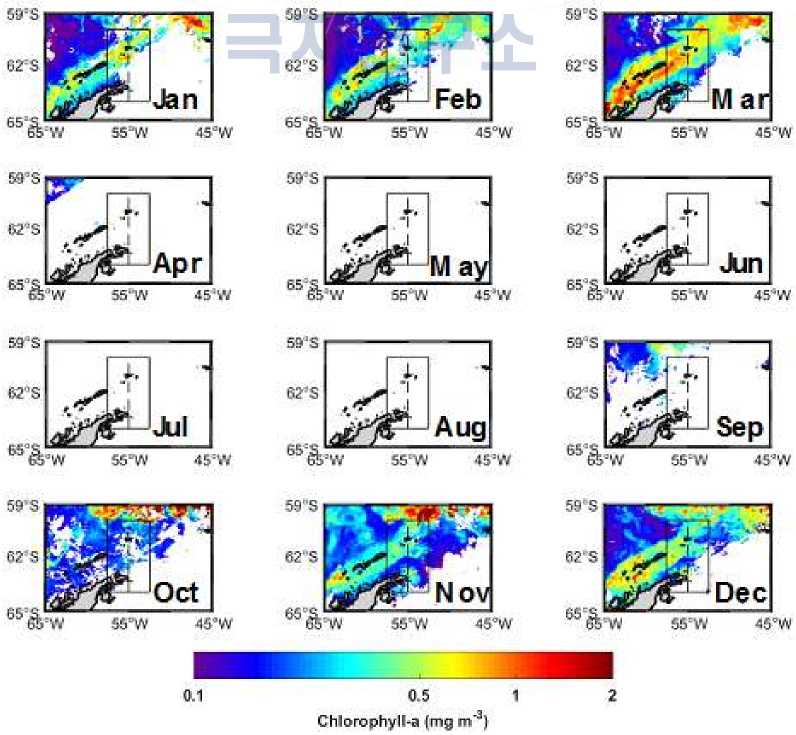

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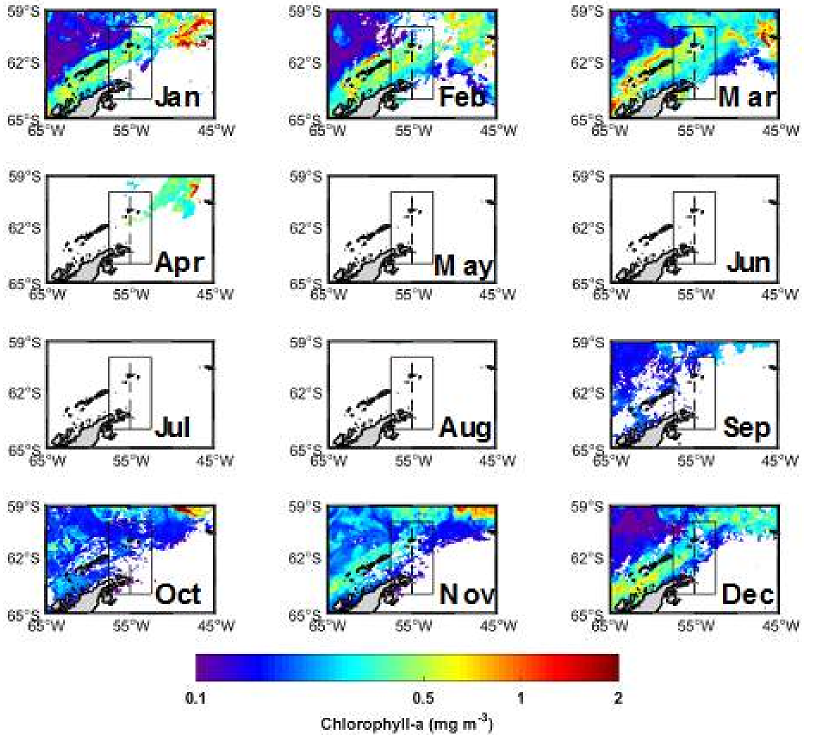

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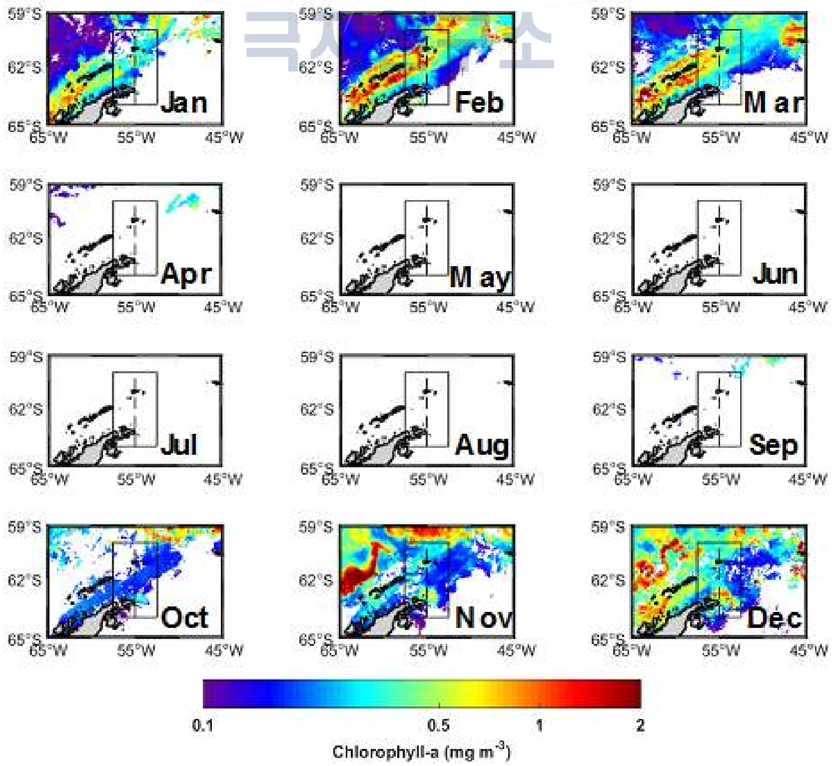

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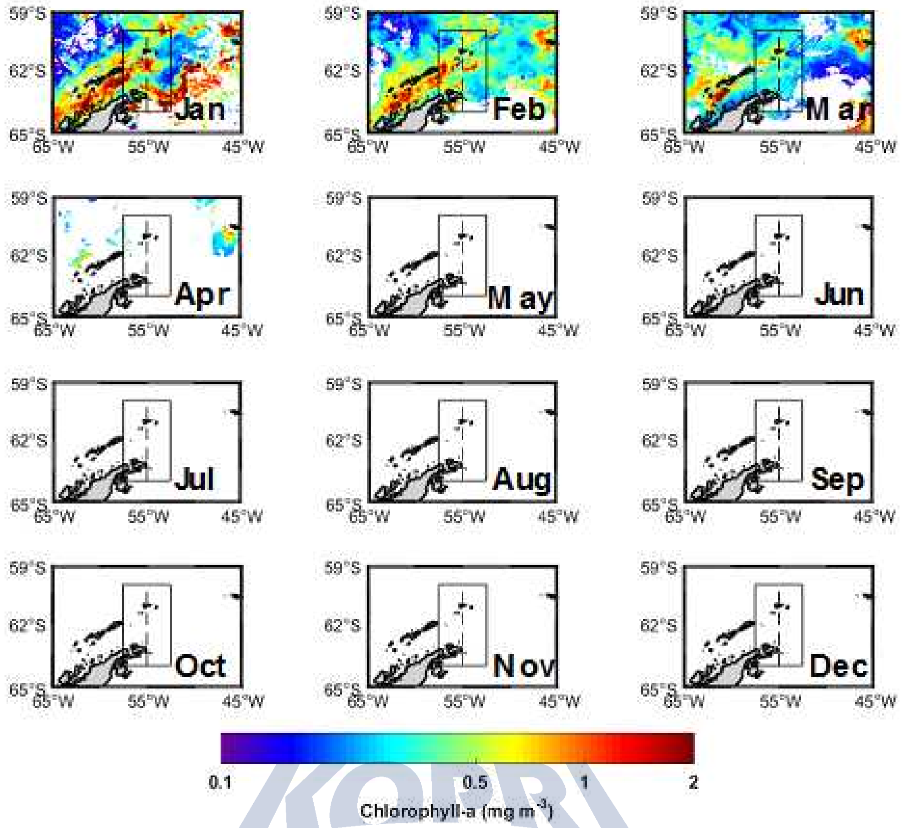

그림 15 월별 엽록소-a 농도 분포(2016년)

2. 과거 Ocean Iron Fertilization 논문

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Ocean Iron Fertilization Experiments: Past–Present–Future with Introduction to Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) Project

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Abstract. Since the start of the industrial revolution, human activities have caused a rapid increase in atmospheric CO_2 concentrations, which have in turn been cited as the cause of a variety climate changes such as global warming and ocean acidification. Various approaches have been proposed to reduce atmospheric CO_2 concentrations. The 'Martin (or Iron) Hypothesis' suggests that ocean iron fertilization (OIF) should be an efficient method for stimulating the biological pump in iron-limited high nutrient-low chlorophyll regions. To test the Martin hypothesis, a total 13 OIF experiments have been performed since 1990 in the Southern Ocean (7 times), in the subarctic Pacific (3 times), in the equatorial Pacific (twice), and in the subtropical Atlantic (once). These OIF field experiments demonstrated that primary production could be significantly increased after artificial iron addition. However, export production efficiency revealed by the OIF experiments was unexpectedly low compared to production from natural processes in all, except one of the experiments (i.e., the Southern Ocean European Iron Fertilization Experiment, EIFEX). These results, including side effects such as N_2O production and hypoxia development, have been scientifically debated amongst those who support and oppose OIF experimentation. In the context of increasing global and political concerns associated with climate change, it is valuable to examine the validity and usefulness of the OIF. We provide a general overview of the OIF experiments conducted over the last 25 years (past), a discussion of OIF considerations including possible side effects (present), and an introduction to the OIF experiment plan currently being designed by Korean oceanographers (future).

Keywords: Ocean Iron Fertilization; High-Nutrient and Low-Chlorophyll regions; Biological Pump; Phytoplankton; Iron

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1 Introduction

Since the start of the industrial revolution, human activities have caused a rapid increase in atmospheric CO_2 from ~280 ppm (pre-industry) to ~400 ppm (present) (http://www.esrl.noaa.gov/), which has in turn led a variety of climate changes such as global warming and ocean acidification (IPCC, 2013) (Fig. 1). As the Anthropocene-climate system has rapidly changed toward the more unpredictable, scientific consensus is that the negative outcomes are a globally urgent issue that should be resolved in a timely manner for the sake of all lives on Earth (IPCC, 1990, 1992, 1995, 2001, 2007, 2013). Various ideas/approaches have been proposed to relieve/resolve the problem of global warming (Matthews, 1996; Lenton and Vaughan, 2009; Vaughan and Lenton, 2011; IPCC, 2014; Leung et al., 2014; Ming et al., 2014), largely based on two categories: (1) reduction of atmospheric CO_2 – ocean fertilization to enhance biological CO_2 uptake and/or direct capture or storage of atmospheric CO_2 through chemically engineered processes, and (2) control of solar radiation – artificial aerosol injection into the atmosphere to augment cloud formation and cloud brightening to elevate albedo (Fig. 2). One of the most attractive methods among the proposed approaches is *ocean fertilization* which targets the drawdown of atmospheric CO_2 by nutrient addition (e.g., iron, nitrogen or phosphorus compounds) to stimulate the phytoplankton growth via the ocean biological pump (ACE, 2015).

The ocean biological pump (*a.k.a.* 'export production') is frequently depicted as a process whereby organic matter produced by phytoplankton during photosynthesis in surface waters is quickly transported to intermediate and/or deep waters (Fig. 3a) (Volk and Hoffert, 1985; De La Rocha, 2007). Although efficiency of the biological pump is mainly controlled by the supply of macro-nutrients (i.e., nitrate, phosphate, and silicate) into the euphotic zone leading to new production (Sarmiento and Gruber, 2006), iron acts as an essential micro-nutrient to stimulate the uptake of macro-nutrients for phytoplankton growth (Fig. 3b) (Martin and Fitzwater, 1988; Martin, 1990; Morel and Price, 2003). In the subarctic Pacific, equatorial Pacific, and Southern Ocean, which are well known as high-nutrient and low-chlorophyll (HNLC) regions (Fig. 4a and b), phytoplankton cannot completely utilize the available macro-nutrients (particularly nitrate) during photosynthesis due to a lack of iron. For this reason, primary production in these HNLC regions is relatively low in spite of the availability of nutrients (Fig. 4a and b).

It is thought, based on Arctic/Antarctic ice core analyses, that atmospheric CO_2 (~180 ppm) during the Last Glacial Maximum (LGM; ~20,000 years ago) was much lower than during pre-industrial times (~280 ppm) (Neftel et al., 1982; Barnola et al., 1987; Petit et al., 1999). Over the last 25 years, several hypotheses have been proposed to explain the mechanisms that lowered atmospheric CO_2 level during the LGM (Broecker, 1982; McElroy, 1983; Falkowski, 1997; Broecker and Henderson, 1998; Sigman and Boyle, 2000). One is particularly relevant to modern nutrient cycling in the Southern Ocean. In 1990, Martin hypothesized an LGM mechanism whereby the biological pump was substantially enhanced due to the relief of iron-limitation in HNLC regions, in particular the Southern Ocean, via high dust inputs (Fig. 3b). These dust inputs are generally regarded as one of major natural iron sources fertilizing oceans. He concluded with the now famous and often cited words "*Give me half a tanker of iron, and I will give you the next ice age*" (Martin, 1990). Since Martin's hypothesis was first published, there has been enormous interest in ocean iron fertilization (OIF) because only a small amount of iron (C:Fe ratios = 100,000:1, Anderson and Morel, 1982) is needed to stimulate a strong phytoplankton response. Therefore, much of the investigative focus has been centered on artificially adding iron to HNLC regions as a means of accelerating the ocean biological pump (ACE, 2008).

To test the Martin's hypothesis, 2 natural and 13 artificial OIF experiments for scientific study have been performed to date in the subtropical Atlantic, equatorial Pacific, subarctic Pacific, and Southern Ocean (Blain et al., 2007; Pollard et al., 2009; Strong et al., 2009) (Fig. 4a and Table 1). These OIF experiments demonstrated that primary production could be significantly increased after iron addition (de Baar et al., 2005; Boyd et al., 2007). High export production/carbon

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sequestration efficiencies were observed from natural OIF experiments in the Southern Ocean near the Kerguelen Plateau and Crozet Islands (Blain et al., 2007; Pollard et al., 2009). However, the artificial OIF experiments showed unexpectedly weak responses compared to natural production in all the experiments (de Baar et al., 2005; Boyd et al., 2007), except one; the Southern Ocean European Iron Fertilization Experiment, EIFEX (Smetacek et al., 2012). These results, which include side effects such as N_2O production and hypoxia development (Fuhrman and Capone, 1991), have been scientifically debated amongst those who support and oppose OIF experimentation (Chisholm et al., 2001; Johnson and Karl, 2002; Lawrence, 2002; Buesseler and Boyd, 2003; Williamson et al., 2012).

In the context of increasing global and political concerns associated with rapid climate change, it is still valuable to examine the validity and usefulness of artificial OIF experimentation as a climate change strategy. Therefore, the purpose of this paper is (1) to provide an overview of the OIF experiments conducted over the last 25 years, (2) to discuss the pros and cons of OIF, including possible side effects, and (3) to introduce the plans for the Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) currently being designed by Korean oceanographers.

2 Past: Overview of artificial OIF experiments

This overview of past OIF experimentation begins in Section 2.1 with a presentation of how each of the experiments was designed and why each was performed. The unique prior ocean conditions for the various experiments are described in Section 2.2. Tracing the OIF effects is described in Section 2.3 and biogeochemical responses to the OIF experiments are presented in Section 2.4.

2.1 Design/Objective of artificial OIF experiments

A total of 13 artificial OIF experiments have been conducted in the following areas: HNLC (i.e., nitrate >10 μM) regions such as the equatorial Pacific (twice), subarctic Pacific (3 times), and Southern Ocean (7 times), and one low-nutrient and low-chlorophyll (LNLC) (i.e., nitrate <10 μM) region, i.e., the subtropical Atlantic (once) (Table 1, Fig. 4a and b).

2.1.1 OIF in the equatorial Pacific

The first OIF experiment, IronEx-1 (Table 1), was carried out over 10 days in October 1993 in the equatorial Pacific (Martin et al., 1994; Coale et al., 1998). This region, located to the south of the Galapagos Islands, was proposed as an optimal place to perform an OIF experiment because (1) the warm temperatures, high light intensity, and low cloud cover allowed for rapid phytoplankton growth, (2) the relatively large number of research cruises conducted in the region provided sufficient physical and biogeochemical property information, (3) it was easily accessible, and (4) it provided an opportunity to examine the natural relationship between primary production and iron addition (via iron inputs into open-ocean waters via the plumes off the western coast of Galapagos Islands) before artificial OIF experiment (Martin and Chisolm, 1992; Martin et al., 1994).

However, the magnitude of biogeochemical responses in IronEx-1 was not as dramatic as expected (Martin et al., 1994). Three hypotheses were advanced to explain the unexpectedly weak results: (1) the possibility of other unforeseen micro-nutrient (e.g., cadmium and manganese) limitations, (2) the short residence time of bioavailable iron in the experimental surface patch due to unstable water-column structure, and (3) the extremely high grazing stress placed on the patch by zooplankton (Cullen, 1995).

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To investigate the unexpected responses revealed in IronEx-1, a second OIF experiment, IronEx-2, was conducted in May 1995 (Coale et al., 1996). The IronEx-2 research cruise occupied generally the same area for a longer period (17 days) providing more time to collect integrated information about the biogeochemical, physiological, and ecological responses to the OIF experiment. IronEx-2 demonstrated that massive phytoplankton blooming associated with OIF in the equatorial Pacific was possible, and it rekindled interest in and stimulated OIF experiments in other HNLC regions (Coale et al., 1996; Bidigare et al., 1999).

2.1.2 OIF in the Southern Ocean

The Southern Ocean, the largest HNLC region in the World Ocean, became the next region selected for OIF experimentation (Frost, 1996) because of its important role in intermediate and deep water formation, which suggested great potential for affecting the carbon sequestration associated with iron addition (Martin, 1990; Sarmiento and Orr, 1991; Cooper et al., 1996; Marshall and Speer, 2012). The Southern Ocean iron release experiment (SOIREE) (Table 1 and Fig. 4a), the first *in situ* OIF experiment performed in the Southern Ocean, took place in February 1999 (13 days) in the Australasian-Pacific sector of the Southern Ocean (Boyd et al., 2000). Iron-induced phytoplankton blooms confirmed that the supply of iron controls primary production in the Southern Ocean. It has also been shown that a model can produce LGM atmospheric CO_2 levels (~200 ppm) using SOIREE results with atmospheric dust flux obtained from the Vostok ice core analysis (Watson et al., 2000). The following year, a second Southern Ocean OIF experiment, EisenEx ('Eisen' is iron in German), was performed in November (23 days) in a closed cyclonic eddy of the Atlantic sector of the Southern Ocean (Smetacek, 2001).

The Southern Ocean exhibits markedly varied silicate concentrations on either side of the Antarctic Polar Front (PF): low silicate concentrations (<5 μM) to the north of the PF (>61° S) and high silicate concentrations (>60 μM) to the south of the PF (<61° S) (Fig. 4c). Silicate-requiring diatoms, which are one of the large-sized phytoplankton groups and have an important role in the biological pump, are responsible for ~75 % of the annual primary production in the Southern Ocean (Tréguer et al., 1995). Therefore, silicate availability is an important factor when considering the enhancement of export production via OIF experimentation. As SOIREE and EisenEx were performed to the south of the PF under intermediate silicate concentration (~5–25 μM) conditions (Boyd et al., 2000; Gervais et al., 2002) (Fig. 4c; Fig. 4a for experiment locations), the interaction between silicate availability and iron addition was not clearly verified. To elucidate this issue, two OIF experiments were conducted during January–February of 2002 in two distinct regions: The Southern Ocean iron experiment-north (SOFeX-N) and -south (SOFeX-S) of the PF (Coale et al., 2004; Hiscock and Millero, 2005) (Table 1).

To measure biologically driven gas fluxes (e.g., CO_2, dimethylsulfide, CO, N_2O, N_2, and O_2), the Surface Ocean Lower Atmosphere Study (SOLAS) Air–Sea Gas Exchange (SAGE) experiment was conducted during March–April 2004 (15 days) in HNLC sub-Antarctic waters (under low silicate concentration) between subtropical region and the PF (Harvey et al., 2010; Law et al., 2011) (Fig. 4c).

Early OIF experiments had not clearly shown whether artificial OIF could effectively reduce atmospheric CO_2 levels through enhancement of the biological pump, i.e., rapid transport of surface organic matter to intermediate/deep waters (Boyd et al., 2007), but the results were interesting enough to spur continued efforts. With the aim of confirming that OIF could increase export production, an experiment known as EIFEX was carried out during February–March 2004 in a PF cyclonic eddy core. With the intention of finding deep export production, EIFEX was a much longer experiment (39 days), compared to earlier attempts (~21 days) (Smetacek et al., 2012). The Indian and German Atlantic sector iron fertilization experiment (LOHAFEX; 'Loha' is iron in Hindi) was conducted during January–March 2009 (40 days) also in a PF cyclonic eddy at the same latitude with EIFEX, but under low silicate concentration (Fig. 4c) again with the aim of investigating an iron fertilized bloom in the surface layer, deep export carbon production, and biomass converted back into CO_2 by bacteria and/or zooplankton (Smetacek and Naqvi, 2010; Martin et al., 2013).

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2.1.3 OIF in the subarctic North Pacific

A strong longitudinal gradient in aeolian dust deposition (i.e., high dust deposition in the west to low in the east), known as natural OIF, has been found in the subarctic North Pacific (Duce and Tindale, 1991). However, there was little information about differences in phytoplankton biomass and communities along the longitudinal dust gradient (Duce and Tindale, 1991; Moore et al., 2002). To investigate the relationship between phytoplankton biomass/community and this dust gradient, the Subarctic Pacific iron Experiment for Ecosystem Dynamics Study-1 (SEEDS-1) was conducted in July–August 2001 (13 days) in the western subarctic gyre using the RV *Kaiyo-Maru* (Tsuda et al., 2003, 2005), and the Subarctic Ecosystem Response to Iron Enrichment Study (SERIES) was performed in July–August 2002 (25 days) in the in the Gulf of Alaska using the RV *John P. Tully*, *El Puma*, and *Kaiyo-Maru* (Boyd et al., 2004, 2005). The main objective of SERIES was to investigate the duration of phytoplankton blooming (i.e., start to finish) after iron addition. Two years later, SEEDS-2 repeated the experiment in almost same location and season with SEEDS-1 using the RV *Hakuho-maru* and *Kilo-Moana* (Tsuda et al., 2007).

2.1.4 OIF in the subtropical North Atlantic

To investigate influence of co-limited iron and phosphate on primary production, the *in situ* PO_4^{3-} and Fe^{2+} addition experiment (FeeP) was conducted by adding both phosphate and iron in LNLC region of the subtropical North Atlantic during April–May 2004 (21 days) using two RV *Charles Darwin* and *Poseidon* (Rees et al., 2007).

2.2 Environmental conditions prior to iron addition

To investigate initial environmental conditions (~1–7 days before iron addition), physical and biogeochemical properties were determined at the sites of the OIF experiments (Steinberg et al., 1998; Coale et al., 1998; Bakker et al., 2001; Boyd and Law, 2001; Gervais et al., 2002; Coale et al., 2004; Boyd et al., 2005; Takeda and Tsuda, 2005; Tsuda et al., 2007; Cisewski et al., 2008; Harvey et al., 2010; Cavagna et al., 2011) (Fig. 6, Table 2 and 3). The OIF experiments were conducted under a wide range of physical conditions in terms of mixed layer depth (MLD) and sea surface temperature (SST).

The MLDs ranged from 10 m (SEEDS-1) to 97.6 m (EIFEX) (Fig. 6c), and were shallower in the equatorial Pacific (mean ± SD = 27.5 ± 2.5 m; SD represents standard deviation) and subarctic Pacific (mean ± SD = 22.7 ± 9.0 m) than in the Atlantic Ocean (FeeP: 40 m) and Southern Ocean (mean ± SD = 56.8 ± 18.9 m). Variation in MLD was highest in the OIF experiments conducted in the Southern Ocean and lowest in those conducted in the equatorial Pacific. MLDs in the experiments performed in the western subarctic Pacific were much shallower in SEEDS-1 (10 m) than in SEEDS-2 (28 m), even though the two experiments were carried out in nearly in the same location and season (Tsuda et al., 2007).

SST at the OIF sites ranged from -0.5 °C (SOFeX-S) to 25.2 °C (IronEx-2) (Fig. 6d). SST was much higher in the OIF experiments conducted in the equatorial Pacific (mean ± SD = 24.1 ± 1.15 °C) and Atlantic Ocean (FeeP: 20.7 °C) than those conducted in the Southern Ocean (mean ± SD = 9.4 ± 2.2 °C) and subarctic Pacific (mean ± SD = 4.9 ± 3.7 °C). Although the two OIF experiments carried out in the equatorial Pacific occurred in different seasons (i.e., IronEx-1: October, IronEx-2: May), the surface physical conditions were quite similar (Steinberg et al., 1998). SOFeX-N/S which were conducted along the same line of longitude in the Southern Ocean exhibited distinct differences in SST; 7.1 °C in SOFeX-N and -0.5 °C in SOFeX-S (Coale et al., 2004). Among the OIF experiments conducted in the Southern Ocean, SAGE carried out in the late summer (late March – early April) had the highest SST (11.5 °C) (Harvey et al., 2010).

Regions for OIF experimentation have usually been selected using preliminary surveys to confirm that the sites were subject to HNLC conditions: high nitrate concentration (>~10 μM) and low chlorophyll-a concentration (<1 mg m^{-3}). Nitrate concentrations ranged from 7.9 μM (SAGE) to 26.3 μM (SOFeX-S) (Fig. 6e and Table 2). Among the various OIF HNLC experiment sites, the equatorial Pacific (i.e., IronEx-1 and IronEx-2) had the lowest initial nitrate concentrations (mean ± SD = 10.6 ± 0.2 μM), while the Southern Ocean had the highest (mean ± SD = 21.2 ± 5.8 μM). One exception to the focus on HNLC study sites was the FeeP experiment which took place in the subtropical North Atlantic, a typically LNLC region (nitrate < 0.01 μM and chlorophyll-a < 1 mg m^{-3}) (Fig. 6e and h, Table 2 and 3).

The full range of initial silicate concentrations for all the OIF experiments is expressed in the Southern Ocean where values ranged widely ranged from 0.83 μM (SAGE) to 62.8 μM (SOFeX-S) (Fig. 6f and Table 2). Generally speaking, however, initial silicate concentrations were lower in the equatorial Pacific (mean ± SD = 4.5 ± 0.6 μM) than in the Southern Ocean (mean ± SD = 15.1 ± 20.4 μM) and subarctic Pacific (mean ± SD = 27.3 ± 9.6 μM). Nevertheless, SOFeX-N, SAGE, and LOHAFEX all conducted in the Southern Ocean were representative of very low-silicate HNLC (HNLCLSi) regions with initial silicate concentrations less than 2.5 μM (Coale et al., 2004; Harvey et al., 2010; Martin et al., 2013).

Phosphate concentrations ranged from 0.01 μM (FeeP) to 1.9 μM (SOFeX-S) (Table 2). Consistent with the World Ocean Circulation Experiment sections and maps (Talley et al., 2007; Koltermann et al., 2011) which suggest increasing surface and near surface nitrate values from Antarctica equatorward, initial Southern Ocean phosphate concentrations were higher to the south 50° S (mean ± SD = 1.6 ± 0.2 μM) than to the north (mean ± SD = 1.1 ± 0.4 μM). They were also higher in the Atlantic sector (mean ± SD = 1.6 ± 0.2 μM) than in the Pacific sector (mean ± SD = 1.0 ± 0.5 μM). Consistent with both the meridional gradient and the basin differences, IronEx in the equatorial Pacific found generally lower initial phosphate values (<1 μM) similar to those seen by SAGE in the southwest Pacific.

Using continuous shipboard measurement systems, OIF experiments have also observed initial surface partial pressure of CO_2 (pCO_2) conditions (Wanninkhof and Thoning, 1993; Steinberg et al., 1998; Bakker et al., 2001; Bakker et al., 2005; Hiscock and Millero, 2005; Takeda and Tsuda, 2005; Smetacek et al., 2005; Wong et al., 2006; Tsumune et al., 2009; Currie et al., 2011). Initial pCO_2 values ranged from 330 ppm (SAGE) to 538 ppm (IronEx-2) (Table 2). Initial pCO_2 values were much higher in the equatorial Pacific (mean ± SD = 504.5 ± 33.5 ppm) than those in the Southern Ocean (mean ± SD = 355.3 ± 12.5 ppm) and subarctic Pacific (mean ± SD = 370 ± 16.3 ppm).

As previously mentioned, the Fv/Fm ratio, a measure of the photosynthetic efficiency of phytoplankton, is widely used to determine the degree to which iron is the limiting nutrient for phytoplankton growth (Fv/Fm ranges from 0 to 1 where conditions are less iron limited condition as Fv/Fm approaches 1) (Boyd et al., 2005). Initial Fv/Fm ratios were less than ~0.3 (Fig. 6g and Table 3) suggesting a tendency for iron limitation. Prior to iron addition, initial chlorophyll-a concentration, measured by fluorometer, ranged from 0.04 mg m^{-3} (FeeP) to 0.9 mg m^{-3} (SEEDS-1) (Fig. 6h and Table 3). However, as was the case for nitrate, compared to all the other OIF experiment sites, FeeP showed unusually low initial chlorophyll-a. The average initial OIF chlorophyll-a concentration was 0.43 ± 0.27 mg m^{-3}. Prior to the OIF experiments, except in SEEDS-1, SOFeX-S, and EIFEX where the diatoms were dominated by micro-plankton (20–200 μm), phytoplankton communities were dominated by pico-plankton (0.2–2.0 μm) and nano-plankton (2.0–20 μm) (Coale et al., 1998; Landry et al., 2000; Boyd and Law, 2001; Gervais et al., 2002; Tsuda et al., 2005; Coale et al., 2004; Boyd et al., 2005; Hoffmann et al., 2006; Harvey et al., 2010; Tsuda et al., 2007; Martin et al., 2013).

2.3 Tracing the effects of iron addition

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Iron(II) and sulfate aerosols are ubiquitous in the atmosphere, and therefore iron-sulfate ($FeSO_4 \cdot H_2O$), a common form of combined iron that enters the ocean environment via dust deposition, has been frequently regarded as a bioavailable iron source for glacial periods (Zhuang et al., 1992; Zhuang and Duce, 1993; Spolaor et al., 2013). In addition, iron-sulfate is a common inexpensive agricultural fertilizer that is relatively soluble in acidified seawater (Coale et al., 1998). Therefore, OIF experiments have been carried out by releasing commercial iron-sulfate dissolved in acidified seawaters into moving ship propeller wash (Fig. 5).

The patch size fertilized by the first iron addition varied from 25 km^2 (e.g., FeeP; iron addition of 1840 kg) to 300 km^2 (e.g., LOHAFEX; iron addition of 2000 kg) (Boyd et al., 2007; Martin et al., 2013) (Table 1 and Fig. 6a and b). In general, background dissolved iron concentrations in the ocean environment are <0.2 nM. During the OIF experiments, dissolved iron concentrations increased to ~1.0–4.0 nM and decreased to background concentrations within days (Table 1). The fast decrease in dissolved iron concentrations indicates that iron-sulfate was transformed chemically into a solid form that readily sticks to other substances. This process occurs more rapidly in warmer waters (ACE, 2015). Therefore, except for the single iron addition experiments of IronEx I, SEEDS-1, and FeeP (Martin et al., 1994; Tsuda et al., 2005; Rees et al., 2007), to maintain an iron-fertilized patch, most of the OIF experiments conducted multiple iron additions at the patch centre. These multiple addition experiments included: (2 additions) EIFEX, SERIES, SEEDS-2, LOHAFEX (Boyd et al., 2005; Smetacek et al., 2012; Martin et al., 2013), (3 additions) IronEx-2, EisenEx, SOFeX-N (Coale et al., 1996; Gervais et al., 2002; Coale et al., 2004; Nishioka et al., 2005), and (4 additions) SOIREE, SOFeX-S, SAGE (Boyd and Law, 2001; Coale et al., 2004; Harvey et al., 2010) (Table 1).

To trace the iron-fertilized patch, OIF experiments used a combination of biogeochemical-based and physical-based approaches. In biogeochemical approaches, the OIF experiments (except EIFEX) used sulfur hexafluoride (SF_6) artificially added as a chemical tracer (Martin et al., 1994; de Baar et al., 2005). SF_6 is useful for investigating physical mixing and advection-diffusion processes in the ocean environment due to its low solubility, nontoxicity, and biogeochemically inert characteristics (Law et al., 1998). Injected SF_6 concentrations were continuously monitored using gas chromatography with an electron capture detector system (Law et al., 1998; Tsumune et al., 2005). Usually only one SF_6 injection was necessary as background levels are generally extremely low in the ocean (<1.2 fM; f: femto-, 10^{-15}) (Law et al., 1998; Law et al., 2006; Martin et al., 2013), however, in the SAGE experiment with higher mixing and lateral dilution, there were three injections (Harvey et al., 2010). Underway sampling systems, measuring biogeochemical parameters such as photosynthetic quantum efficiency (Fv/Fm, where Fm is the maximum chlorophyll fluorescence yield and Fv is the difference between Fm and the minimum chlorophyll fluorescence yield), pCO_2, and chlorophyll fluorescence, were also used in the fertilized patch as alternative means of following the patch (Gervais et al., 2002; Boyd et al., 2005; Tsuda et al., 2007; Harvey et al., 2010; Smetacek et al., 2012).

In physically based approaches, surface-drifting buoys equipped with Array for Real-time Geostrophic Oceanography (ARGO) and Global Positioning System (GPS) sensors have been used to map moving fertilized patches in space and time (Coale et al., 1998; Boyd and Law, 2001; Law et al., 2006; Martin et al., 2013). Buoy position can be transmitted to the ship every 5–10 min. The NASA-airborne oceanographic lidar aircraft have also been employed to assess the large-scale effects of iron addition on surface chlorophyll in the fertilized patch compared to surrounding regions (Martin et al., 1994).

2.4 Biogeochemical responses

The biogeochemical responses to a wide range of iron addition (350–4000 kg) via OIF experiments in the HNLC regions were surveyed over periods ranging from 10–40 days (Table 1 and Fig. 6b). The initial response was a rapid increase of Fv/Fm ratio generally observed within the first 24 hours after iron addition. This was not the case in SEEDS-1 and SEEDS-2 where a detectable increase was observed 3–5 days later. The maximum post-iron-addition Fv/Fm ranged from 0.31 (SEEDS-1) to 0.65 (SOIREE and SOFeX-S) and Fv/Fm generally reached values of 0.5 or greater (Table 3 and Fig. 7a). The increase in Fv/Fm ratio after iron addition suggests that phytoplankton response to iron enrichment is prompt, and results support the hypothesis that natural phytoplankton growth in these HNLC regions is iron-limited (Boyd and Abraham, 2001; Gervais et al., 2002; Tsuda et al., 2003; Boyd et al., 2005; Barber and Hiscock, 2006; Tsuda et al., 2007; Peloquin et al., 2011; Croot et al., 2008; Martin et al., 2013).

Depletion of macro-nutrients in fertilized patches provides indirect evidence that phytoplankton growth in surface waters is driven by iron fertilization (Boyd and Law, 2001). Significant nitrate uptake (i.e., ΔNitrate = $[NO_3^-]_{post\text{-}fertilization} - [NO_3^-]_{pre\text{-}fertilization} < 0$) occurred in all the OIF experiments, except SAGE (Table 2 and Fig. 7b) (Martin et al., 1994; Boyd et al., 2000; Hiscock and Millero, 2005; Law et al., 2011). Negative ΔNitrate ranged from -0.7 μM in the equatorial IronEx1 experiment to -15.8 μM in SEEDS-1. However, in SAGE, concentrations of macro-nutrients in the iron fertilized patch exceeded the initial concentrations (i.e., ΔNitrate > 0) due to the physical processes such as deepened mixed layer depth and lateral advection of high nutrient waters (Table 2 and Fig. 7b) (Law et al., 2011).

Changes in surface water chlorophyll-a concentrations are a direct indication of the effect of iron addition on phytoplankton growth (Fig. 7c). Generally, chlorophyll-a concentrations increased substantially 2- to 20-fold with max values of ~0.1 mg m^{-3} (FeeP) to 22 mg m^{-3} (SEEDS-1) (Fig. 7c and Table 3) when nitrate concentrations sharply decreased from 3–5 days after iron addition (Tsuda et al., 2003; Coale et al., 2004; Boyd et al., 2004; Tsuda et al., 2007; Peloquin et al., 2011; Smetacek et al., 2012). SEEDS-1 and SEEDS-2, performed under similar conditions, presented similar initial chlorophyll-a concentrations (0.8 mg m^{-3}), but their responses to iron addition were different. Iron-stimulated max chlorophyll-a concentration in SEEDS-2 (~2.5 mg m^{-3}) was much lower than those of SEEDS-1 (~22 mg m^{-3}) (Tsuda et al., 2007). Satellite observations were used to spatially and temporally map OIF phytoplankton response (Boyd et al., 2000; Coale et al., 2004; Boyd et al., 2005; Westberry et al., 2013). Sea-viewing Wide Field-of-view Sensor (SeaWiFS) and MODerate resolution Imaging Spectrometer (MODIS) Terra Level-2 chlorophyll-a images showed that increased chlorophyll-a concentrations after iron addition were appeared at ~28 days after iron addition in the SOFeX-N with a long thread shape (1.0 mg m^{-3}) and at ~20 days in the SOFeX-S over somewhat broad area (0.4 mg m^{-3}) (Fig. 7d) (Westberry et al., 2013).

Using both microscopes and high performance liquid chromatography pigment analysis, changes in phytoplankton community effected by iron addition were also investigated. During IronEx-2, SOIREE, EisenEx, SEEDS-1, SOFeX-S, SERIES, and EIFEX, the dominant phytoplankton community tended to shift from pico- and nano-plankton to micro-plankton, resulting in diatom-dominated phytoplankton blooming, a key component for biological pump enhancement (Landry et al., 2000; Boyd and Law, 2001; Gervais et al., 2002; Tsuda et al., 2005; Coale et al., 2004; Boyd et al., 2005; Hoffmann et al., 2006; Harvey et al., 2010). However, there were no observations on taxonomic shift toward diatom-dominated phytoplankton communities in other OIF experiments (Coale et al., 1998; Coale et al., 2004; Rees et al., 2007; Tsuda et al., 2007; Peloquin et al., 2011; Martin et al., 2013). As noted above, the SEEDS-1 and SEEDS-2 experiments were carried out under similar ocean conditions. Nevertheless, SEEDS-2, which resulted in a minimal increase in chlorophyll-a (< 3 mg m^{-3}), was also subject to extensive copepod (meso-zooplankton; 200–2000 μm) grazing (~5 times greater than in SEEDS-1) and therefore did not produce a prominent diatom bloom (Tsuda et al., 2007).

Associated with the OIF-induced phytoplankton blooms, the magnitude of primary productivity integrated from

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surface to euphotic depth in iron fertilized patches also became significantly elevated compared to initial levels (i.e., $\Delta PP = PP_{post-fertilization} - PP_{pre-fertilization}$, where PP is primary productivity). Increases in ΔPP ranged from 360 mg C m^{-2} d^{-1} (SAGE) to 1800 mg C m^{-2} d^{-1} (IronEx-2) with maximum values of 790 mg C m^{-2} d^{-1} (EisenEx) to 2430 mg C m^{-2} d^{-1} (IronEx-2) (Fig. 7e and Table 3). As a result of increased ΔPP, drawdown of pCO_2 (negative ΔpCO_2: air→sea) was enhanced during the all OIF experiments except SAGE (Fig. 7f). In SAGE, physical mixing caused an increase in macro-nutrients (positive ΔNitrate, Fig. 7b), which resulted in a reversed pCO_2 pattern (positive ΔpCO_2: sea→air) (Currie et al., 2011). The largest ΔpCO_2 change occurred in SEEDS-1 conducted in the subarctic North Pacific. It also produced the largest ΔNitrate and the greatest chlorophyll increase (Fig. 7f) (Tsuda et al., 2003; de Baar et al., 2005). Overall, OIF ΔpCO_2 reductions ranged from -6 ppm (SEEDS-2) to -130 ppm (SEEDS-1) (Table 2 and Fig. 7f), and were associated with DIC decreases of 6 μM (IronEx-1) to 58 μM (SEEDS-1) (Steinberg et al., 1998; Bakker et al., 2001; Bakker et al., 2005; Boyd et al., 2007; Berg et al., 2011; Currie et al., 2011).

Early OIF experiments showed that iron addition stimulates the first step of biological pump, promotion of phytoplankton growth. To determine whether the second step of biological pump, export of carbon to the deep sea (i.e., increased export production), is enhanced after iron addition, sediment trap and chemical tracers such as natural radiotracer thorium-234 (^{234}Th; half-life = 24.1 days) have been used together and/or individually to estimate the export flux of particulate organic carbon (Bidigare et al., 1999; Nodder et al., 2001; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013). ^{234}Th has a strong affinity for suspended particles, and the extent of ^{234}Th removal in the water column is indicative of the export production below the euphotic zone associated with surface primary productivity (Buesseler, 1998). During IronEx-2, ^{234}Th deficiency was evident in the iron fertilized patch indicating iron-stimulated export production, however there were no ^{234}Th observations conducted in as unfertilized patch for comparison (Bidigare et al., 1999) (Fig. 8b). During EIFEX, initial export flux estimated using ^{234}Th in the upper 100 m of the fertilized patch was 340 mg C m^{-2} d^{-1}. This value remained constant for 25 days after iron addition (Fig. 8a). Then, between 30 and 36 days after iron addition, a massive increase of export flux as high as 1692 mg C m^{-2} d^{-1} was observed in the fertilized patch, while the initial value remained constant in the unfertilized patch (Smetacek et al., 2012). That being said, EIFEX was the exception. Significant changes in export production were not found in any of the other OIF experiments, suggesting that the effect of iron addition on this component of the biological pump remains a question that needs to be resolved possibly by future OIF experimentation (Bidigare et al., 1999; Nodder et al., 2001; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013).

3 Present: OIF debates and considerations

3.1 Environmental side effects

OIF has been proposed as one potential way (*a.k.a.* 'Carbon Capture Storage') of rapidly and efficiently reducing atmospheric CO_2 levels at relatively minimal cost (Buesseler and Boyd, 2003). Over the past 25 years, controlled OIF experiments have illustrated that substantial increases in phytoplankton biomass can be instigated in HNLC regions through iron addition that results in the drawdown of DIC and macronutrients (de Baar et al., 2005; Boyd et al., 2007; Smetacek et al., 2012; Martin et al., 2013). However, the effectiveness of enhancement in this export production, which results in a net transfer of CO_2 from the atmosphere to the ocean intermediate/deep layer (i.e., 'biological pump'), is not yet fully understood or quantified as it appears to vary with region, season, and, as yet unknown factors (Smetacek et al., 2012). Therefore, it is uncertain whether OIF has the potential to sequester CO_2 at a significant rate (~1 Gt of CO_2 per year). In the

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meantime, there are possible environmental side effects in response to iron addition, such as production of greenhouse gases (e.g., N_2O and CH_4) (Lawrence, 2002; Liss et al., 2005; Law, 2008), development of hypoxia/anoxia in water column (Sarmiento and Orr, 1991), and toxic algal blooms (e.g., *Pseudo-nitzschia*) (Silver et al., 2010; Trick et al., 2010), that have been seen and should be addressed before artificial OIF is conducted. These OIF experiment side-effects may themselves effect climate and ecosystem changes that have unexpected negative outcomes (Fuhrman and Capone, 1991). Therefore, it is not surprising that the OIF validation and usefulness has been a subject of debate (Williamson et al., 2012).

OIF experiments have measured climate-relevant gases (i.e., N_2O, CH_4, dimethylsulfide, and halogenated volatile organic compounds) that are produced by biological activity and/or photochemical reaction (Liss et al., 2005) to investigate change before and after iron addition. CH_4 has been considered to be relatively low risk as most of the CH_4 formed in the ocean is used as energy source for microorganisms and is converted to CO_2 before reaching to the sea surface (Smetacek and Naqvi, 2008; Williamson et al., 2012). On the other hand, the ocean is already a significant source for atmospheric N_2O, so any enhancement of biological production that might enhance N_2O emission could work to increase atmospheric greenhouse gas levels rather than decrease them (Bange, 2006). During the SOIREE experiment, a significant increase in N_2O production was observed in the pycnocline after iron addition (Law and Ling, 2001). This phenomenon was also illustrated in a modeling study of long-term and large-scale OIF (Jin and Gruber, 2003). Complicating the story, however, excess N_2O was not found after iron addition during EIFEX, the second-longest experiment (~39 days) (Walter et al., 2005).

Decomposition of iron addition-enhanced biomass may cause decrease oxygen concentrations in the subsurface waters (Williamson et al., 2012). Box model solutions have further suggested that anoxic conditions may develop after OIF (Sarmiento and Orr, 1991). Although mid-water oxygen depletion has not been reported during the OIF experiments to date, it has been suggested that OIF-induced oxygen depletion may be occurred by increased downward carbon exports that elevate microbial respiration (Fuhrman and Capone, 1991).

Dimethylsulfide (DMS), hypothesized to be a precursor of sulfate aerosols that cause cloud formation and so climate cooling, was measured during all OIF experiments (Lawrence, 2002). Significant increases in DMS production were found in some of the OIF experiments (i.e., IronEx-2, SOIREE, EisenEx, and SOFeX-N) (Turner et al., 1996; Turner et al., 2004; Wingenter et al., 2004; Liss et al., 2005). In particular, DMS production increased 6.5-fold after iron addition during SOIREE (Turner et al., 2004). However, there were no significant changes in DMS production after iron addition during IronEx-1, SEEDS-1, and SEEDS-2, despite increases in primary production (Turner et al., 1996; Takeda and Tsuda, 2005; Nagao et al., 2009). In the SERIES experiment, DMS production decreased due to the relatively high bacterial dimethylsulfoniopropionate (DMSP) metabolism (Levasseur et al., 2006), which is precursor of DMS production.

Halogenated volatile organic compounds (HVOCs, such as CH_3Cl, CH_3Br, and CH_3I), well known for their ability to destroy ozone in the lower stratospheric ozone and marine boundary layer (Solomon et al., 1994), were also measured during the OIF experiments (Wingenter et al., 2004; Liss et al., 2005). During SOFeX-N experimentation, iron addition results for HVOC were complicated: CH_3Cl concentrations remained unchanged; CH_3Br concentrations increased by ~14 %; and while generally CH_3I concentrations decreased by ~23 % (Wingenter et al., 2004). CH_3I concentrations increased 2-fold in EisenEx (Liss et al., 2005).

The change of phytoplankton community after iron addition discussed in Section 2.4 also has unintended consequences (Silver et al., 2010; Trick et al., 2010). *In situ* measurements and ship-board culture experiments showed that iron enrichment stimulated growth of the toxigenic diatom genus '*Pseudo-nitzschia*', known to produce neurotoxin domoic acid (DA) that has detrimental marine ecosystem impacts (Trick et al., 2010). For example, during IronEx-2 and SOFeX-S, diatoms belonging to the genus '*Pseudo-nitzschia*' dominated the phytoplankton community and high levels of DA were produced (45 ng of DA l^{-1} in IronEx-2 and 220 ng of DA l^{-1} in SOFeX-S; Silver et al., 2010). However, no DA was found during EisenEx, even though generally '*Pseudo-nitzschia*' was the dominant diatom bloom species (Gervais et al., 2002; Assmy et al., 2007).

The direct and indirect environmental consequences of OIF remain unresolved due to inconsistent, highly uncertain outcomes (Williamson et al., 2012; Johnson and Karl, 2002; Chisholm et al., 2001), suggesting that we haven't yet reached the conclusion of OIF experimentation as a carbon removal strategy (Boyd et al., 2007). Therefore, evaluation and prediction are paramount. It continues to be a valuable exercise to attempt to answer scientific questions about the efficiency of OIF as a means of reducing atmospheric CO_2 as well as to quantify the possible OIF side effects.

3.2 Designing future OIF experiments: Direction and Considerations

Scientific research on OIF has focused on improving our understanding of the efficiency, capacity, and risks of OIF as an atmospheric CO_2 removal strategy. Although the first OIF experiments took place more than twenty years ago, the legal and economic aspects of such a strategy in terms of international laws of the sea and carbon offset markets are not yet clear (ACE, 2015). It is therefore of paramount importance that future OIF experiments continue to focus on the efficiency and capacity of OIF as a means of reducing of atmospheric CO_2, but in doing so should carefully consider major factors such as amount/patch size associated with iron addition (i.e., 'How'), location (i.e., 'Where'), and timing (i.e., 'When') to build on the results of OIF experiments as to develop our understanding of the magnitude and sources of uncertainties and in so doing build confidence in our ability to reproduce results.

How: The first consideration for a successful OIF experiment lies in the strategy/approach. IronEx-1 is a good example of a successful OIF experiment. The IronEx-1 patch was fertilized with acidified iron(II) sulfate and was subsequently traced with large variety of physical-biogeochemical techniques and parameters such as GPS and ARGO equipped drifting buoys, SF_6, Fv/Fm ratio, pCO_2, and chlorophyll fluorescence using underway sampling systems (Martin et al., 1994). Many subsequent OIF experiments adopted the methods introduced from the IronEx-1, and were similarly able to detect environmental changes through the observation of both physical and biogeochemical parameters before and after iron addition (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000; Tsuda et al., 2005; Coale et al., 2004; Boyd et al., 2004; Smetacek et al., 2012). This success suggests that there is no need to completely redesign OIF experimentation as the previous designs and methods are a good reference for future efforts.

Where: The second consideration for a successful OIF experiment is the selection of location. To easily and efficiently observe iron-induced changes, it is important to isolate the iron-fertilized patch from the surrounding unfertilized waters (Coale et al., 1996). Ocean eddies provide an excellent setting for OIF experimentation as they have physically rotating water column structures, that naturally tend to isolate interior waters from the surrounding waters. Mesoscale eddies range from 25–250 km in diameter and maintain their characteristics for 10–100 days after formation (Morrow and Traon, 2012). Eddy centers, in which fertilization is performed, tend to be subject to relatively slow current speeds compared to the surrounding environment with the vertical coherence (Smetacek and Naqvi, 2008). Iron additions were carried out at the center of eddies in EisenEx, EIFEX, and LOHAFEX conducted in the Southern Ocean (Smetacek, 2001; Smetacek and Naqvi, 2008; Smetacek and Naqvi, 2010; Smetacek et al., 2012). Observations were also made outside the eddy core well away from the iron-fertilized patch to provide similar information about environmental conditions to compare with patch observations. EIFEX showed a clear difference in export carbon flux between waters within the patch and external to the patch (Smetacek et al., 2012). Therefore, finding of an appropriate eddy setting in a study area should be one of the high priority considerations in conducting an OIF experiment (Smetacek and Naqvi, 2008).

When: The third consideration for successful OIF experiment is timing which can be broken down into when an experiment starts and how long it lasts. Primary production in ocean environment is generally limited by nutrient availability and/or by light availability, often referred to as single- or co-limitation. Primary production in the Southern Ocean, a representative HNLC region, is subject to co-limitation by micro-nutrients (i.e., iron) and light availability (Mitchell et al., 1991). Previous Southern Ocean OIF experiments have been conducted from spring to late summer, and revealed that during this time of year primary production is limited by iron supply rather than light availability (de Baar et al., 2005; Smetacek and Naqvi, 2008; Peloquin et al., 2011).

Duration: Although it has been reported that the periods that phytoplankton blooms have been maintained by OIF have lasted from ~10 to 40 days (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000; Tsuda et al., 2005; Coale et al., 2004; Boyd et al., 2004; Smetacek et al., 2012), it has also been suggested that most OIF experiments did not cover the full response times from onset to termination (Boyd et al., 2005). For example, SOIREE and SEEDS-1, had relatively short observation periods (~13 days) and saw increasing trends in primary production throughout the experiments (Fig. 9a) suggesting that the observation period should have been extended. Furthermore, after the end of SOIREE, ocean color satellite images showed continued high chlorophyll-a concentrations (~1 mg m^{-3}) in the iron fertilized patch, which was seen as a long ribbon shape that extended some ~150 km for ~46 days; (~7 weeks) after the initial iron addition (Fig. 9b) (Abraham et al., 2000). This result indicates that short experiment periods may not be sufficient for detecting the full influence of artificial iron addition on primary production (Fig. 8b) (Boyd et al., 2000; Tsuda et al., 2003; de Baar et al., 2005). Among OIF experiments, EIFEX, the second-longest at ~39 days, fully monitored all the phases of the phytoplankton bloom from onset to termination, and it alone observed iron-induced deep export production (Fig. 8a and 9a) (Assmy et al., 2013; Smetacek et al., 2012). It is therefore important to predict both the needed time for onset and the time required for the response to run its full course, otherwise it will not be possible to quantify the net effect.

To date, assessment of the effectiveness of OIF has been limited by the small area of the fertilized patches (25–300 km^2) used in the experiments (Fig. 6a). Patch sizes have been limited in part due to the time and expense of comparing fertilized and unfertilized areas (ACE, 2008). However, since these small-scale OIF experiments have demonstrated considerable potential for easily and efficiently reducing atmospheric CO_2 levels, several commercial companies (e.g., GreenSea Venture and Climos, http://www.greenseaventure.com; http://www.climos.com) have been promoting large-scale commercial OIF experiments as a climate mitigation strategy and a means to gain carbon credits (Chisholm et al., 2001; Buesseler and Boyd, 2003). However, this effort has not been able to move forward because the large uncertainties remaining in the technique mean that potential risks to the environment/ecosystem by even small-scale OIF experiments are not yet well understood. At present, large-scale and/or commercial OIF experiments are banned by international regulation (Williamson et al., 2012). The international Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter (London Convention, 1972) and Protocol to the London Convention (London Protocol, 1996) placed legal restrictions on dumping of wastes and other matter that cause hazard, harm, and damage in the ocean and/or interfere with the marine environment. In 2007, the London Convention & Protocol (LC/LP) scientific groups released a statement of concern about ocean fertilization and recommended that ocean fertilization activities be evaluated carefully to ensure that such operations were not contrary to the aims of the LC/LP. Under the LC/LP, commercial activities are prohibited, and only "small-scale" legitimate scientific research in "coastal waters" is allowed (Resolution LC-LP.1 (2008), 2008). LC/LP also developed an assessment framework for scientific ocean fertilization research to be applied on a case-by-case basis founded on the agreed definition and compliance with the aims and objectives of Resolution LC-LP.1 (2008) (Fig. 10) (Assessment Framework for Scientific Research Involving Ocean Fertilization, 2010). This framework demands preliminary scientific research to get a permission for OIF experimentation as transparent/reasonable scientific rationale/purpose and risk analysis undertaken using parameters such as problem formulation, site selection, exposure assessment, effects assessment, risk characterization, and risk management must be provided (Assessment Framework for Scientific Research Involving Ocean Fertilization, 2010). Monitoring is also required an integral component of all approved (i.e., legitimate) scientific research activity to assess ecological impacts and to review actual versus intended geoengineering benefits (ACE, 2015). In October 2013, LC/LP categorized artificial ocean fertilization as marine geoengineering, thereby prohibiting operational OIF activities, but enabling OIF scientific research that meets the permit conditions through the environmental assessment framework (Resolution LP.4 (8), 2013).

4. Future: Introduction to the Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) project

4.1 Background for KIFES

The last artificial OIF experiment, LOHAFEX was led by scientists from CSIR-National Institute of Oceanography in Goa, Alfred-Wegener Institute for Polar and Marine Research (AWI) in Bremerhaven, and 5 other nations. The German government suddenly halted LOHAFEX just before the departure of RV *Polarstern* from the port following protests by NGOs and environmentalists against OIF experimentation due to concern about direct and long-term side effects of artificial iron fertilization on marine ecosystem. To data, only OIF experiment with a scientific and legal review processes was 'LOHAFEX' conducted in the Southern Ocean. Although people are still worried about side effects of OIF and scientists are still curious about the measurable effects of OIF on the ocean environment, there have been no further intensive investigations to fill the gap between supporters and opponents of OIF as the geoengineering approach since LOHAFEX. There are still many unknowns to be investigated about OIF experiments.

The paleoclimate team at Korea Polar Research Institute (KOPRI) found the geological evidence of intensive organic carbon burial in the sediments, which removes atmospheric CO_2, in the eastern Bransfield Basin on the Antarctic Peninsula. The diatomaceous ooze layer was well preserved in the buried sediments of the Bransfield Basin, and represents the fast sinking of diatoms within a short time. Scientists at KOPRI suspect that enhancement of diatom flux might be related to input of bioavailable iron that controls phytoplankton population in the Southern Ocean. In addition, the oceanographic (physical-biogeochemical-geological) parameters might be ascribed to the unique increase of diatom production, the fast sinking rate of the organic matters, and the well preservation of organic carbon in this area. Therefore, it is expected that OIF in diatom-dominated eastern Bransfield Basin will be effective for carbon export. However, the exact driving force for this unique process should be intensively investigated prior to the OIF experiment.

Timely, a science-oriented iron fertilization project, KIFES (Fig. 11), was launched by the Korean oceanographers in 2016 with the research funding supported by the Korean Ministry of Oceans and Fisheries. This project will be led mainly by KOPRI with domestic collaborators (i.e., Incheon National University, Inha University, Pusan National University, Hanyang University, and Yeonsei University) and strengthened by international collaborators (i.e., AWI, Institute of Geological and Nuclear Sciences, MIT-WHOI, University of Otago, University of California at Irvine, McMaster University, University of South Florida, Royal Netherlands Institute for Sea Research, and Dalhousie University). The main purpose of the KIFES project is (1) to further understand the role of iron for atmospheric carbon sequestration in the Southern Ocean, (2) to verify proper environmental conditions to maximize effectiveness of OIF experiment, and (3) to reveal short- and long-term side effects derived from artificial OIF experiment.

4.2 KIFES Plans

The KIFES project is 5-year plan project (2016–2020). This project includes two preliminary environmental surveys, a preliminary OIF test, the KIFES OIF experiment, and an assessment of the KIFES project. In this section, we introduce the major goals and main tasks of KIFES project.

4.2.1 First project year (2016-underway)

Goals: Determination of KIFES OIF experiment sites and establishment of an international OIF network

Main tasks: (1) Investigation of earlier OIF locations and experiments to produce a database of physical and biogeochemical parameters from *in situ* observations and remote-sensing data to select appropriate sites and to determine timing for an new OIF experiment in the eastern Bransfield Strait, (2) Preparation of scientific instruments for ocean physical and biogeochemical monitoring, (3) Establishment of an international collaborative OIF network, and (4) KIFES proposal preparation for approval of LC/LP.

4.2.2 Second project year (2017)

Goal: First preliminary survey to provide a foundational understanding of ocean environmental conditions in the eastern Bransfield Strait

Main tasks: (1) Using ice breaker RV *ARAON*, field investigation of physical and biogeochemical parameters, including side effect parameters such as N_2O in the eastern Bransfield Strait – parameters and sites based on the 2016 investigation, and (2) Continued preparation of LC/LP proposal.

4.2.3 Third project year (2018)

Goals: Second preliminary survey and a preliminary test of OIF in eddy structure prior to KIFES

Main tasks: (1) Detection of an eddy using observations from acoustic Doppler current profilers and satellites in the eastern Bransfield Strait, (2) Intensive physical and biogeochemical field investigation in the eddy, (3) Rehearsal of OIF experiment in the eddy structure, and (4) Submission of the LC/LP proposal to obtain approval for the KIFES experiment from International Maritime Organization.

4.2.4 Fourth-year project (2019)

Goal: KIFES – OIF experiment in an eddy structure (Fig. 11)

Main tasks: (1) The conducting of KIFES, a scientific OIF experiment in an eddy structure in the eastern Bransfield Strait employing underway sampling systems, multiple sediment traps, sub-bottom profilers, sediment coring systems, and satellite observations, and (2) Assessment for KIFES effects and side effects

4.2.5 Fifth-year project (2020)

Goal: Integrated assessment of the KIFES project

Main tasks: (1) Submission of the OIF assessment report, (2) Submission of scientific results to international journals, (3) Collection of feedback about the KIFES project from international scientific/oceanographic communities, and (4) Preparation of the second stage of the KIFES project.

4.3 Expected results of KIFES

KIFES will be performed after a decade long gap since LOHAFEX. None of the KIFES scientists have any interest in selling carbon credits by conducting OIF experiments. Rather, our interest lies in the detailed investigation of the biogeochemical effects of iron addition in the Southern Ocean and in the OIF evaluation as one of possible geo-engineering methods that might be used to mitigate the realities of the climate change effects we face. We hope that the 5-year KIFES project can give a clear answer as to whether or not OIF is a promising as a geo-engineering solution. The KIFES project will provide fundamental information and guidelines for future OIF experiments in HNLC regions. In particular, the aforementioned risks and side effects of OIF will be thoroughly investigated so as to belay international concern. Likewise, international cooperation is essential for the successful performance of KIFES and for improvement of our outlook for the Earth's future.

5 Summary

To test the Martin's hypothesis, a total 13 artificial OIF experiments for scientific study were conducted in the HNLC regions during the last 25 years. The biogeochemical responses to OIF experiments were observed in the increases of primary production as a result of drawdowns of macro-nutrients and DIC. In most experiments, dominance of phytoplankton group tended to be shifted from small-sized groups to large-sized groups, resulting in diatom-dominated phytoplankton community. However, the effectiveness in export production enhancing ocean biological pump was not clearly confirmed by the OIF experiments, except in one, EIFEX. Likewise, the possible environmental side effects in response to iron addition, such as production of greenhouse gases, development of hypoxia/anoxia in water column, and toxic algal blooms were not fully evaluated due to inconsistent outcomes with large uncertainty depending on OIF experiment conditions and settings. Therefore, validation and suitability of artificial OIF for mitigation of increasing atmospheric carbon levels has been debated. To fully understand the efficiency, capacity, and risks of OIF, scientifically-based and site-limited OIF experimentation is needed to consider such major factors as amount/patch size associated with iron addition, location, and experiment length, including compliance with international OIF regulations. A timely 5-year iron fertilization project, KIFES was launched in 2016 under the leadership of KOPRI with the support of domestic/international collaborative networks. This project focuses on investigating the details of the biogeochemical responses to artificial iron addition in the Southern Ocean and assessing suitability of OIF as one possible carbon removal strategy under international maritime laws. Previously raised issues associated with the risks of OIF will be investigated during the KIFES project.

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Table 1. Summary of OIF experiments; time, location, research vessel, amounts of Fe addition (day of Fe addition from the beginning of OIF experiment), background Fe concentrations, Fe concentrations after Fe additions, tracer, patch size fertilized by first Fe addition, experiments periods, and characteristics of study regions.

	Experiment	Time	Location	Research Vessel	Fe (kg) (day)	Initial Fe (nM)	After Fe (nM)	Tracer	Patch size (km^2)	Period (days)	Region
1	IronEx-1	Oct 1993	5° S, 90° W Equatorial Pacific	RV *Columbus Iselin*	①450 (0)	0.06	3.60	SF_6	64	10	HNLC
2	IronEx-2	May 1995	3.5° S, 104° W Equatorial Pacific	RV *Melville*	①225 (0) ②112 (3) ③112 (7)	0.02	2.00 1.00 1.00	SF_6	72	17	HNLC
3	SOIREE	Feb 1999	61° S 141° E Southern Ocean- Australasian-Pacific sector	RV *Astrolab*	①768 (0) ②312 (3) ③312 (5) ④353 (7)	0.08	3.80 2.60 2.60 2.50	SF_6	50	13	HNLC
4	EisenEx	Nov 2000	48° S, 21° E Southern Ocean- Atlantic sector	RV *Polarstern*	①780 (0) ②780 (7) ③780 (16)	0.06	2.00	SF_6	50	23	HNLC
5	SEEDS-1	Jul–Aug 2001	48.5° N, 165° E North Pacific- Western subarctic gyre	RV *Kaiyo-Maru*	①350 (0)	0.05	2.90	SF_6	80	13	HNLC
6	SOFeX-N	Jan–Feb 2002	56.23° S, 172° W Southern Ocean- Atlantic sector	RV *Revelle* RV *Melville*	①631 (0) ②631 (5) ③450 (30)		1.20	SF_6	225	40	HNLCLSi
7	SOFeX-S	Jan–Feb 2002	66.45° S, 171.8° W Southern Ocean- Atlantic sector	RV *Revelle* RV *Melville* RV *Polar star*	①315 (0) ②315 (4) ③315 (7) ④315 (11)		0.70	SF_6	225	28	HNLC
8	SERIES	Jul-Aug 2002	50.14° N, 144.75° W North Pacific- Eastern subarctic Pacific	RV *John P. Tully* RV *El Puma* RV *Kaiyo Maru*	①315 (0) ②315 (6)	<0.10	2.00 0.60	SF_6	77	25	HNLC

To be continued

	Experiment	Time	Location	Research Vessel	Fe (kg) (day)	Initial Fe (nM)	After Fe (nM)	Tracer	Patch size (km^2)	Period (days)	Region
9	EIFEX	Feb–Mar 2004	50° S, 2° E Southern Ocean-Atlantic sector	RV *Polarstern*	①1406 (0) ②1406 (13)	0.20	1.50 0.34		167	39	HNLC
10	FeeP	Apr–May 2004	27.5° N 22.5° W North Atlantic-Subtropical north-east Atlantic	RV *Charles Darwin* RV *Poseidon*	①1840 (0)	0.20	3.00	SF_6	25	21	LNLC
11	SAGE	Mar–Apr 2004	46.7° S 172.5° E Southern Ocean-Southeast of New Zealand	RV *Tangaroa*	①265 (0) ②265 (6) ③265 (9) ④265 (12)	0.09	3.03 1.59 0.55 1.01	SF_6	36	15	HNLCLSi
12	SEEDS-2	Jul–Aug 2004	48° N, 166° E North Pacific-Western subarctic gyre	RV *Hakuho-Maru* RV *Kilo-Moana*	①332 (0) ②159 (6)	0.17	1.38	SF_6	64	26	HNLC
13	LOHAFEX	Jan–Mar 2009	48° S, 15° W Southern Ocean-Atlantic sector	RV *Polarstern*	①2000 (0) ②2000 (21)		2.00	SF_6	300	40	HNLCLSi
1	CROZEX*	Nov 2004–Jan 2005	44° S, 50° E Southern Ocean-South of sub-Antarctic Front	RV *Discovery*		0.04	0.55				HNLC
2	KEOPS*	Jan–Feb 2005	50° S, 73° E Southern Ocean-South of Polar Front	RV *Marion Dufresne*							HNLC

* Natural OIF experiments

Sources are as follows: Martin et al., 1994; Coale et al., 1996; Coale et al., 1998; Boyd et al., 2000; Gervais et al., 2002; Tsuda et al., 2003; Boyd et al., 2004; Bakker et al., 2005; Boyd et al., 2005; Coale et al., 2004; de Baar et al., 2005; Hiscock and Millero, 2005; Nishioka et al., 2005; Tsuda et al., 2005; Tsumune et al., 2005; Boyd et al., 2007; Rees et al., 2007; Tsuda et al., 2007; Harvey et al., 2010; Law et al., 2011; Smetacek et al., 2012; Martin et al., 2013.

Table 2. Changes of chemical parameters from initial to after concentrations by OIF experiments. Note that *ΔDIC represents changes in DIC concentrations (i.e., $[DIC]_{post\text{-}fertilization} - [DIC]_{pre\text{-}fertilization}$).

	Experiment	Initial NO_3 (μM)	After NO_3 (μM)	Initial PO_4 (μM)	After PO_4 (μM)	Initial Si (μM)	After Si (μM)	Initial pCO_2 (ppm)	After pCO_2 (ppm)	*ΔDIC (μM)
1	IronEx-1	10.8	10.1	0.92	0.90	3.9	3.88	471	458	-6
2	IronEx-2	10.4	6.4	0.80	0.55	5.1	1.1	538	465	-27
3	SOIREE	25.0	22.0	1.50		10.0	7.0	350	312–318	-(18–15)
4	EisenEx	22.0	21.0	1.60	1.5	10.0	10.0	360	340–342	-(15–12)
5	SEEDS-1	18.5	2.7		0.44	31.8	5.0	390	260	-58
6	SOFeX-N	21.9	20.5	1.40	1.31	2.5	1.4	367	341	-13
7	SOFeX-S	26.3	22.8	1.87	1.66	62.8	58.8	365	329	-21
8	SERIES	10.0–12.0	3.0	>1.00	<0.50	14.0–16.0	<2.0	350	265	-36
9	EIFEX	25.0	23.5	1.80	1.50	19.0	8.0	360	330	-13.5
10	FeeP	<0.01		0.01						<-1
11	SAGE	7.9–10.3	11.8	0.62–0.85		0.83–0.97		330	338	25
12	SEEDS-2	18.4	12.7			36.1		370	364	
13	LOHAFEX	20.0	17.5	1.30	1.10	0.50–1.40				

Sources are as follow: Martin et al., 1994; Steinberg et al., 1998; Boyd et al., 2000; Bakker et al., 2001; Bakker et al., 2005; Hiscock and Millero, 2005; Smetacek et al., 2005; Takeda and Tsuda, 2005; Wong et al., 2006; Boyd et al., 2007; Tsumune et al., 2009; Harvey et al., 2010; Smetacek and Naqvi, 2010; Berg et al., 2011; Currie et al., 2011; Law et al., 2011.

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Table 3. Changes of biological parameters from initial to after (maximum) concentrations by OIF experiments. Note that *PP (mg C m^{-2} d^{-1}) was estimated by multiplying PP (mg C m^{-3} d^{-1}) with mixed layer depth (m).

	Experiment	Initial Fv/Fm	Maximum Fv/Fm	Initial Chlorophyll (mg m^{-3})	Maximum Chlorophyll (mg m^{-3})	Initial PP (mg C m^{-2} d^{-1})	Maximum PP (mg C m^{-2} d^{-1})
1	IronEx-1	0.30	0.60	0.24	0.65	300–450*	805–1330*
2	IronEx-2	0.25	0.50	0.15–0.20	4.00	630	2430
3	SOIREE	0.22	0.65	0.25	2.00	120	1300
4	EisenEx	0.30	0.56	0.50	2.50	130–220	790
5	SEEDS-1	0.19	0.31	0.80–0.90	21.8	420	1670
6	SOFeX-N	0.20	0.5	0.15	2.60	144	1500
7	SOFeX-S	0.25	0.65	0.30	3.80	216	972
8	SERIES	0.24	0.55	0.35	5.00	300	2000
9	EIFEX	0.28	0.6	0.70	3.16	750	1500
10	FeeP			0.04	0.07		
11	SAGE	0.27	0.61	0.63	1.33	540	900
12	SEEDS-2	0.29	0.40	0.80	2.48	390	1000
13	LOHAFEX	0.33	0.40–0.50	0.50	1.25	960	1560

Sources are as follow: Kolber et al., 1994; Martin et al., 1994; Behrenfeld et al., 1996; Steinberg et al., 1998; Boyd et al., 2000; Boyd and Law, 2001; Gervais et al., 2002; Coale et al., 2004; Boyd et al., 2005; de Baar et al., 2005; Takeda and Tsuda, 2005; Tsuda et al., 2005; Assmy et al., 2007; Boyd et al., 2007; Tsuda et al., 2007; Kudo et al., 2009; Harvey et al., 2010; Berg et al., 2011; Currie et al., 2011; Peloquin et al., 2011; Smetacek et al., 2012; Thiele et al., 2012; Martin et al., 2013; Latasa et al., 2014.

Figure Captions

Fig. 1. Diagram showing the monthly atmospheric CO_2 concentrations (ppm) (blue) according to the Mauna Loa Observatory, Hawaii (http://www.esrl.noaa.gov/gmd/ccgg/trends/data.html), global monthly land surface air and sea surface temperature anomalies (°C) (red) (http://data.giss.nasa.gov/gistemp/), and pH (green) measured at station ALOHA in the central Pacific (http://hahana.soest.hawaii.edu/hot/products/HOT_surface_CO2.txt). The data values represent moving average values for 12 months and shading indicates the standard deviation of 12 months.

Fig. 2. Schematic representation of several proposed climate-engineering methods (modified from Matthews, 1996).

Fig. 3. The iron hypothesis as suggested by Martin (1990). (a) Efficiency of the biological pump under normal conditions and (b) efficiency of the biological pump as a result of Fe enrichment. DIC is dissolved inorganic carbon and OM is organic matter (modified from Sarmiento and Gruber, 2006).

Fig. 4. Global annual distribution of surface (a) chlorophyll concentrations (mg m^{-3}), (b) nitrate concentrations (μM), and (c) silicate concentrations (μM). Chlorophyll-a concentration distribution represents the Aqua MODIS chlorophyll-a composite from July 2002 to February 2016 (http://oceancolor.gsfc.nasa.gov/cgi/l3), while the nitrate and silicate distributions were presented by Ocean Data View program (https://odv.awi.de) using the World Ocean Atlas 2013 dataset (https://odv.awi.de/en/data/ocean/world_ocean_atlas_2013). White circles indicate the locations of 13 artificial OIF experiments and black triangles indicate the locations of natural OIF experiments. Note that the numbers indicate the order of experiments (see Table 1).

Fig. 5. Pictures for iron addition procedures: (a) Iron(II) sulfate of 7000 kg, (b) hydrochloric acid, (c) tank system for mixing with Iron(II) sulfate, hydrochloric acid, and seawater, (d) outlet pipe connected with tank system, (e) pumping iron into prop wash during EIFEX (Smetacek, 2015). (f) Discharging of Iron(II) sulfate (http://www.geoengineeringmonitor.org/reasons-to-oppose/).

Fig. 6. (a) Patch size (km^2) for first Fe addition (blue bar) and maximum patch size (sky blue bar) during OIF experiments. (b) Amounts (kg) of first Fe addition (blue bar) and total Fe addition (sky blue bar). (c) Minimum (blue bar) and maximum (sky blue bar) mixed layer depth (m). (d) Average sea surface temperature (°C). Initial (e) nitrate concentrations (μM), (f) silicate concentrations (μM), (g) Fv/Fm ratio, and (h) chlorophyll-a concentrations (mg m^{-3}) before iron addition. Note that the numbers indicate the order of experiments (see Table 1). Sources are as follows: Kolber et al., (1994); Martin et al., (1994); Behrenfeld et al., (1996); Coale et al., (1996); Steinberg et al., (1998); Boyd et al., (2000); Boyd and Law, (2001); Gervais et al., (2002); Coale et al., (2004); Boyd et al., (2004); Boyd et al., (2005); de Baar et al., (2005); Hiscock and Millero, (2005); Takeda and Tsuda, (2005); Tsuda et al., (2005); Assmy et al., (2007); Boyd et al., (2007); Tsuda et al., (2007); Harvey et al., (2010); Berg et al., (2011); Law et al., (2011); Peloquin et al., (2011); Smetacek et al., (2012); Thiele et al., (2012); Martin et al., (2013); Latasa et al., (2014).

Fig. 7. (a) Initial (coral bar) and maximum (light coral bar) Fv/Fm ratio during OIF experiments. (b) Changes in nitrate concentrations (ΔNitrate = $[NO_3^-]_{post\text{-}fertilization} - [NO_3^-]_{pre\text{-}fertilization}$; μM). (c) Initial (coral bar) and maximum (light coral bar) chlorophyll-a concentrations (mg m^{-3}). (d) Distributions of chlorophyll-a concentrations (mg m^{-3}) at ~28 days after iron addition in the SOFeX-N and at ~20 days in the SOFeX-S. White dotted box indicates phytoplankton bloom during OIF experiments. Changes in (e) primary productivity ($\Delta PP = [PP]_{post\text{-}fertilization} - [PP]_{pre\text{-}fertilization}$; mg C m^{-2} d^{-1}) and in (f) pCO_2 ($\Delta pCO_2 = [pCO_2]_{post\text{-}fertilization} - [pCO_2]_{pre\text{-}fertilization}$; ppm). Color bar indicates changes in DIC ($\Delta DIC = [DIC]_{post\text{-}fertilization} - [DIC]_{pre\text{-}fertilization}$; μM). Note that PP (mg C m^{-2} d^{-1}) of OIF experiment number 1 (IronEx-1) was estimated by multiplying PP (mg C m^{-3} d^{-1}) with mixed layer depth and the numbers indicate the order of experiments (see Table 1). Sources are as follows: Kolber et al., (1994); Martin et al., (1994); Behrenfeld et al., (1996); Coale et al., (1996); Steinberg et al., (1998); Boyd et al., (2000); Bakker et al., (2001); Boyd and Law, (2001); Gervais et al., (2002); Coale et al., (2004); Boyd et al., (2004); Bakker et al., (2005); Boyd et al., (2005); de Baar et al., (2005); Hiscock and Millero, (2005); Smetacek et al., (2005); Takeda and Tsuda, (2005); Tsuda et al., (2005); Wong et al., (2006); Assmy et al., (2007); Boyd et al., (2007); Tsuda et al., (2007); Kudo et al., (2009); Tsumune et al., (2009); Harvey et al., (2010); Smetacek and Naqvi, (2010); Berg et al., (2011); Currie et al., (2011); Law et al., (2011); Peloquin et al., (2011); Smetacek et al., (2012); Thiele et al., (2012); Martin et al., (2013); Latasa et al., (2014).

Fig. 8. Time-series of (a) ^{234}Th-derived particulate organic carbon (POC) fluxes (mg m^{-2} d^{-1}) of the upper 100 m layer in patch (coral bar) and outside patch (blue bar) during EIFEX (modified from Smetacek et al., 2012). Time-series of (b) vertically integrated ^{234}Th (dpm l^{-1}) in patch (coral circle) and outside patch (blue diamond) relative to parent ^{238}U (dpm l^{-1};

dotted black line) during SOIREE (modified from Nodder et al., 2001).

Fig. 9. (a) Time-series of mixed layer depth-integrated chlorophyll-a concentrations (mg m^{-2}) during SOIREE (pink line), SEEDS-1 (brown line), SERIES (cyan line), SEEDS-2 (blue line), and EIFEX (teal line). Sources are as follows: Boyd and Abraham, (2001); Tsuda et al., (2007); Assmy et al., (2013). (b) The distributions of chlorophyll-a concentrations (mg m^{-3}) in ~5 days and ~46 days during SOIREE from SeaWiFS Level-2 daily images.

Fig. 10. Assessment framework for scientific research involving ocean fertilization (OF) (modified from Assessment Framework for Scientific Research Involving Ocean Fertilization, 2010).

Fig. 11. Schematic diagram of KIFES representing experiment target site (eddy structure) and survey methods (underway sampling systems, multiple sediment traps, sub-bottom profilers, sediment coring systems, and satellite observations).

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Fig. 1

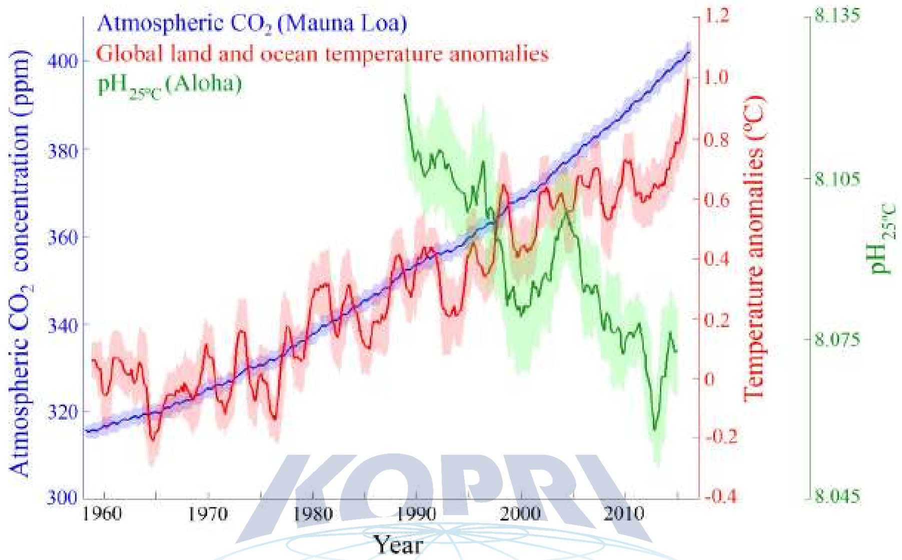

Fig. 2

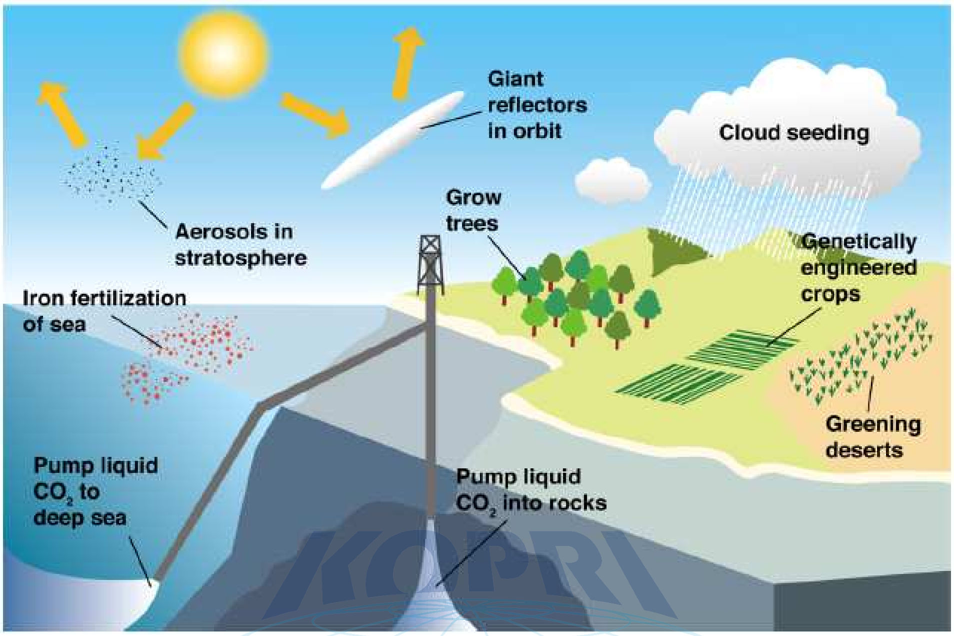
Giant reflectors in orbit
Cloud seeding
Aerosols in stratosphere
Grow trees
Genetically engineered crops
Iron fertilization of sea
Greening deserts
Pump liquid CO2 to deep sea
Pump liquid CO2 into rocks

Fig. 3

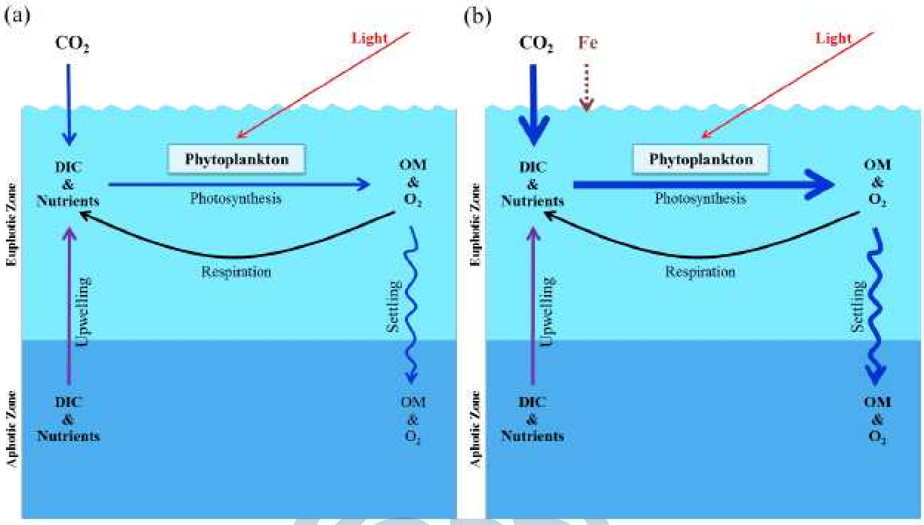
(a)
CO2
Light
Phytoplankton
DIC & Nutrients
OM & O2
Photosynthesis
Respiration
Upwelling
Settling
Euphotic Zone
Aphotic Zone
DIC & Nutrients
OM & O2
(b)
CO2
Fe
Light
Phytoplankton
DIC & Nutrients
OM & O2
Photosynthesis
Respiration
Upwelling
Settling
Euphotic Zone
Aphotic Zone
DIC & Nutrients
OM & O2

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Fig. 4

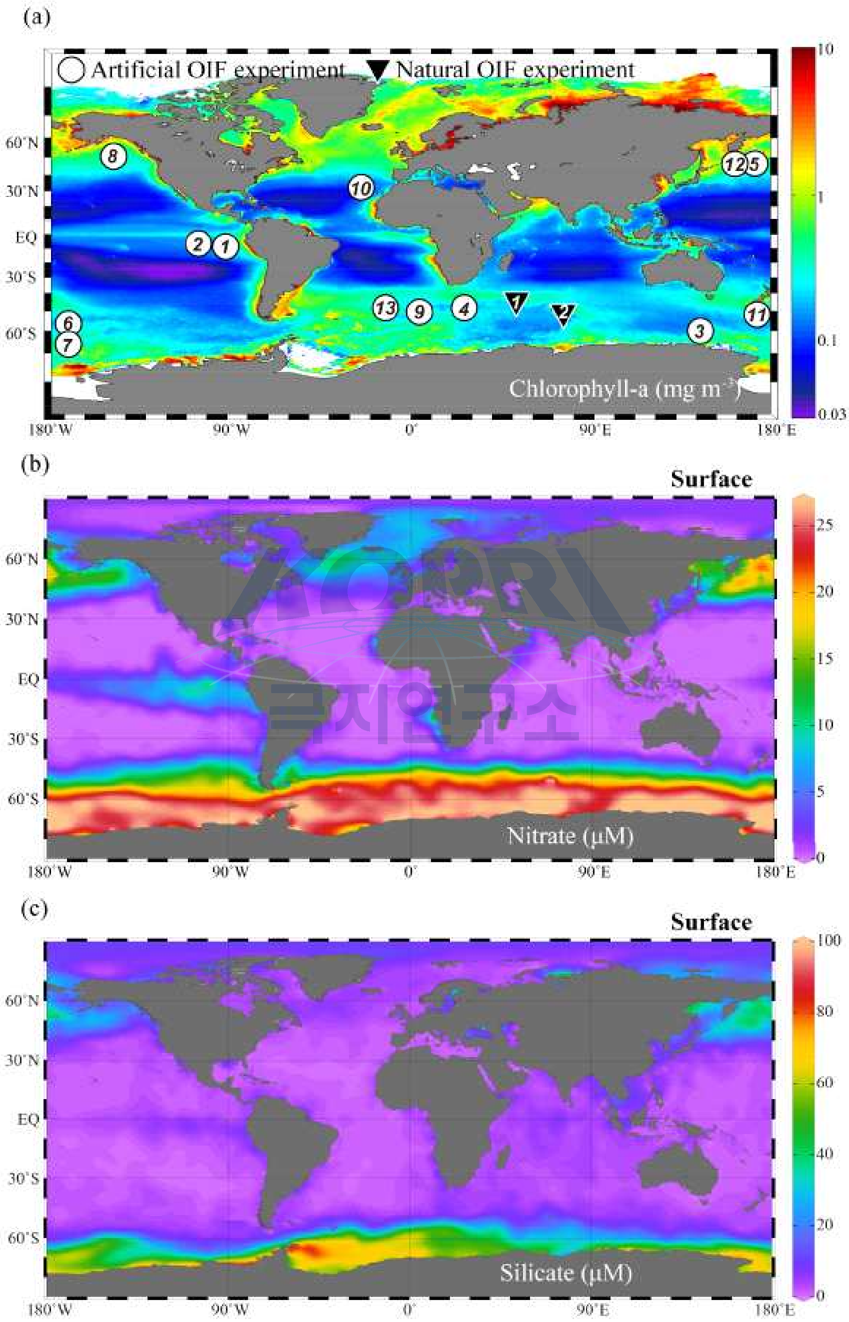

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Fig. 5

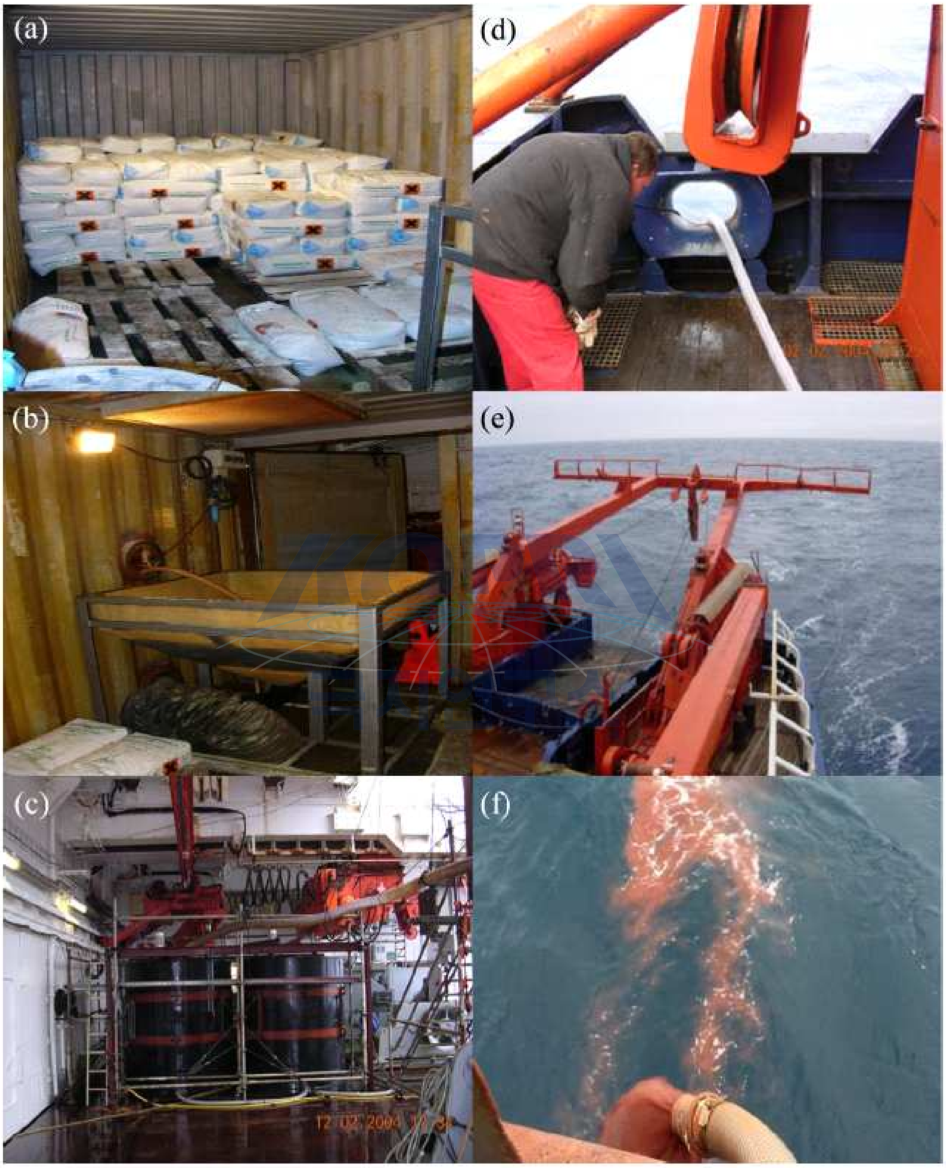

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Fig. 6

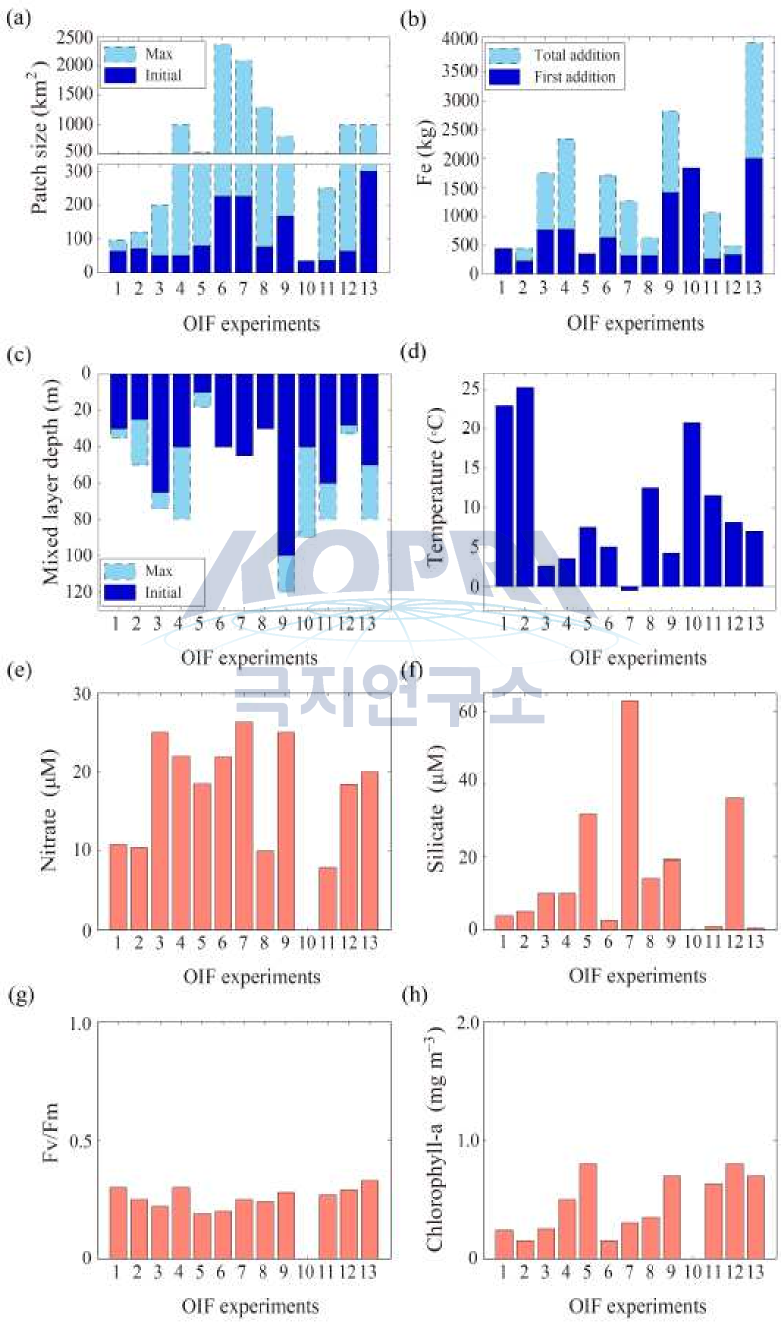

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Fig. 7

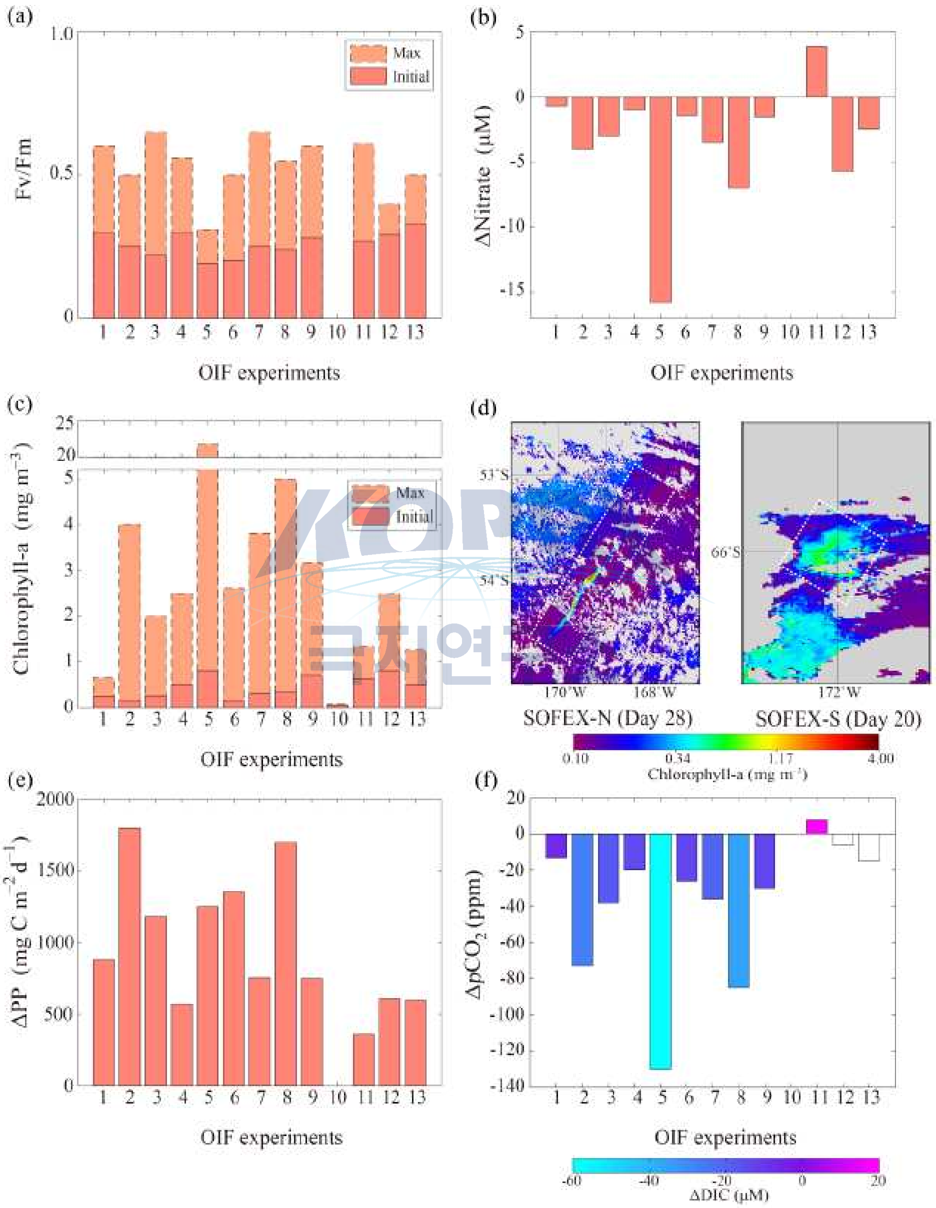

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Fig. 8

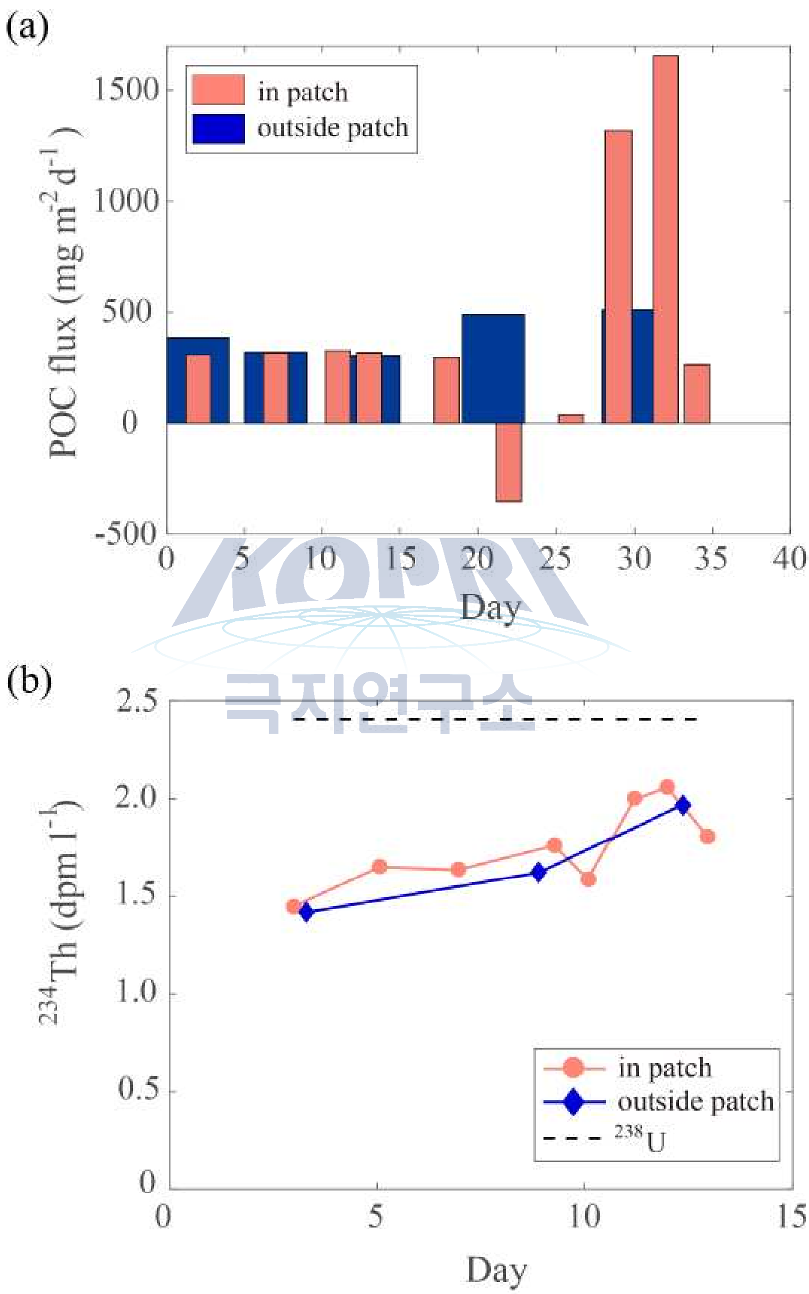

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Fig. 9

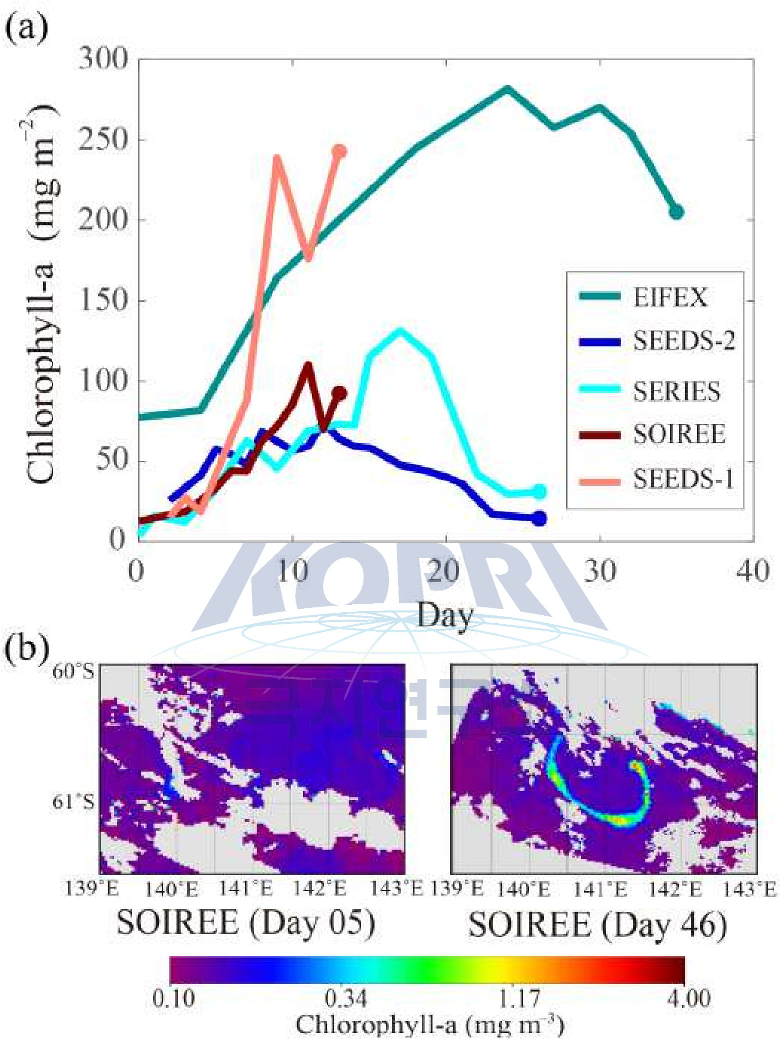

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Fig. 10

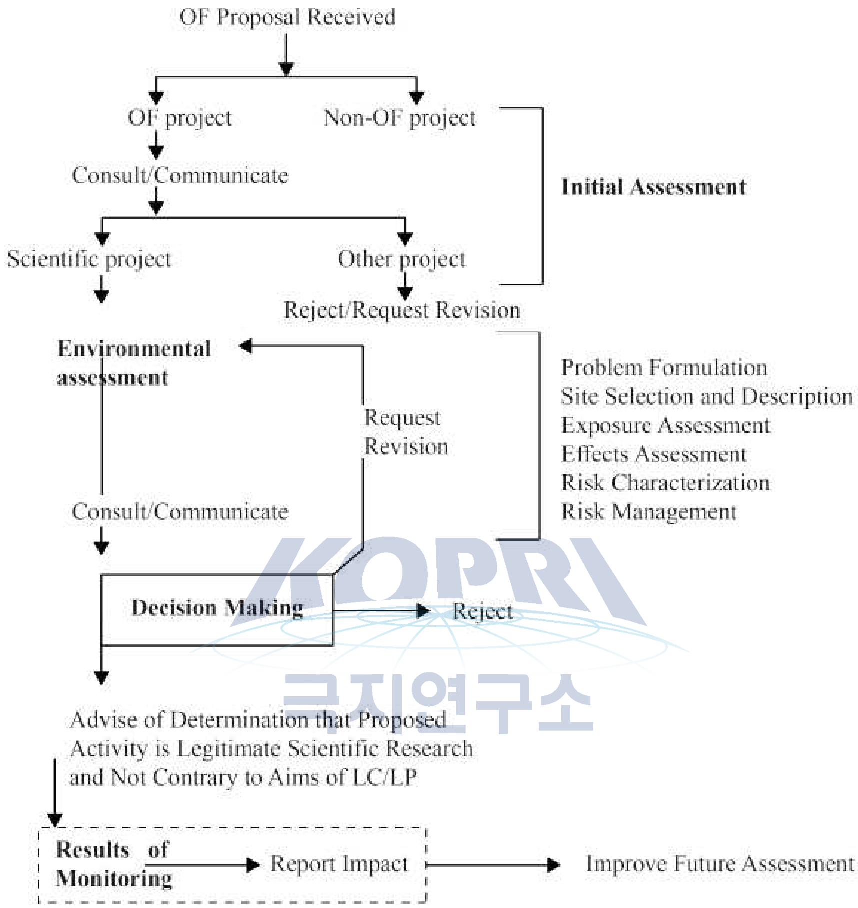
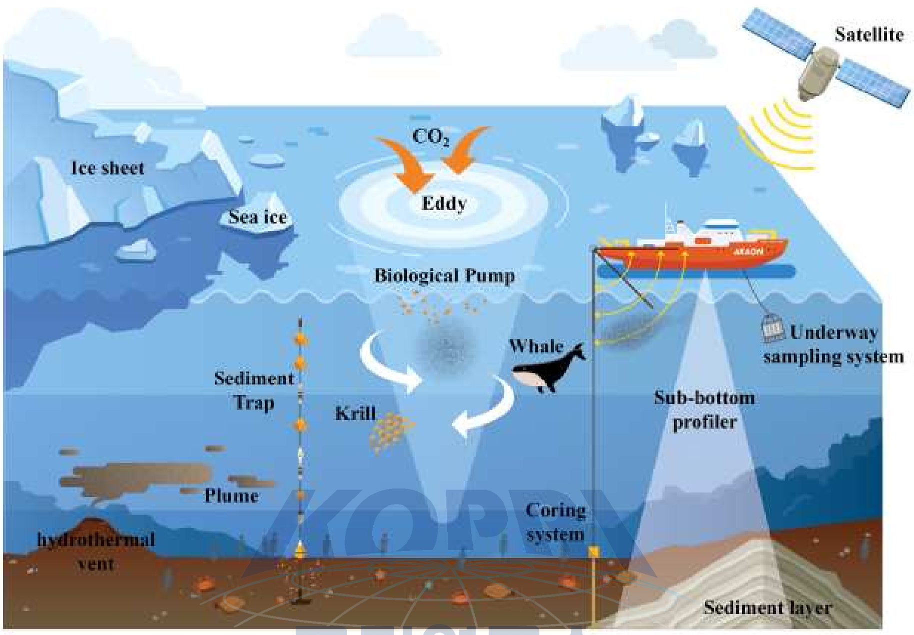


Fig. 11


Satellite
CO_2
Ice sheet
Eddy
Sea ice
Biological Pump
Underway sampling system
Whale
Sediment Trap
Krill
Sub-bottom profiler
Plume
Coring system
hydrothermal vent
Sediment layer

주 의

1. 이 보고서는 극지연구소 위탁과제 연구결과보고서 입니다.
2. 이 보고서 내용을 발표할 때에는 반드시 극지연구소에서 위탁연구과제로 수행한 연구결과임을 밝혀야 합니다.
3. 국가과학기술 기밀유지에 필요한 내용은 대외적으로 발표 또는 공개하여서는 안됩니다.