CNI세미나2020-004

안정동위원소 활용 역량강화 세미나

기후변화대응연구센터

충청남도 서해안기후환경연구소

2020. 2. 24.

충남연구원
ChungNam institute

세부 프로그램

시간	주요내용	
15:00~15:10 (10‘)	개회 및 소개	
15:10~15:50 (40‘)	① ICP-AES & ICP-MS를 이용한 분진의 금속 원소 분석	신형선 박사
15:50~16:30 (40‘)	② 안정동위원소 기기 활용 (EA-IRMS 관련, 원산지 판별)	봉연식 박사
16:30~17:10 (40‘)	③ 납 동위원소 분석 및 산지 추정 연구 활용	정연중 박사
17:10~18:00 (50‘)	종합토의 및 폐회	이상신 센터장

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ICP-AES & ICP-MS를 이용한 분진의 금속원소 분석

신형선 (한국기초과학지원연구원)

ICP-AES & ICP-MS를 이용한 분진의 금속원소분석

신 형 선

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KOREA BASIC SCIENCE INSTITUTE

무기 원소분석

- 원자흡수 분광법 (AAS)
- 유도결합플라즈마 원자방출법 (ICP-AES)
- 유도결합플라즈마 질량분석법(ICP-MS)
- X-선 형광분석법 (XRF)
- - 기타 표면분석법 및 플라즈마 (DCP, CMP)분석기

Comparison of AAS, ICP-AES and ICP-MS

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	AAS	ICP-AES	ICP-MS
Detection Limit	> 수 ppb	Sub – ppb ~ 수 ppb	수 ppt ~ 수십 ppt
Precision	~ 1 %	1 % ~ 2 % (< 5 %)	1 % ~ 3 % (< 5 %)
분석시간	< 1 min/element	1 min ~ 5 min/sample	1 min/sample
Total Dissolved solid	1 % ~ 3 %	2 % ~ 20 % (1 % ~ 3 %)	0.1 % ~ 0.5 % (< 0.2 %)
Interference	Chemical Spectral	Spectral	Mass
정성 및 반정량	No	Yes	Yes
Isotope analysis	No	No	Yes
Operation	Easy	Slightly difficult	Difficult
시료 소모량	Very high	High (low)	Low
특징	Alkali metal (K, Na)	Transition metal	Heavy metal, REE

Temperature Regions of the ICP

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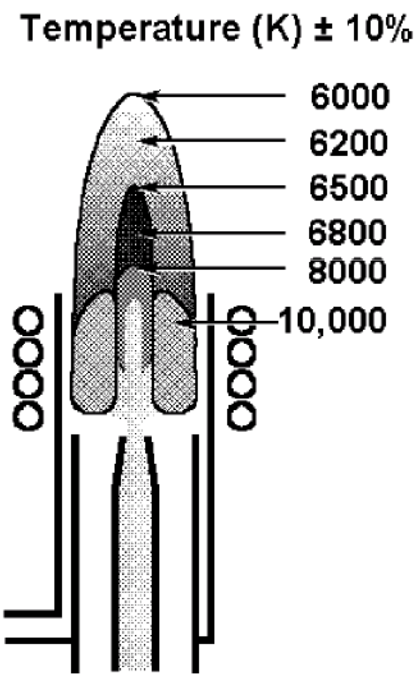


Atomic Spectroscopy

Atom line transitions		
Elements	($E=hc/\lambda$) excitation potential (eV)	wavelength (nm)
S	6.85	180.73
Zn	5.79	213.86
Cu	3.81	324.75
Na	2.10	589.59
K	1.61	769.90

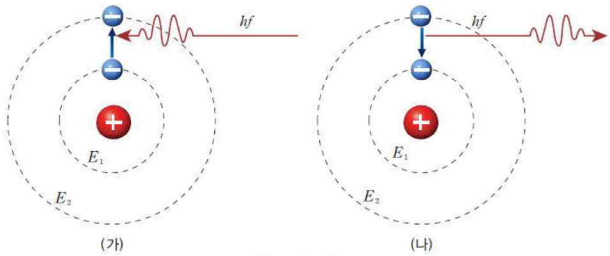
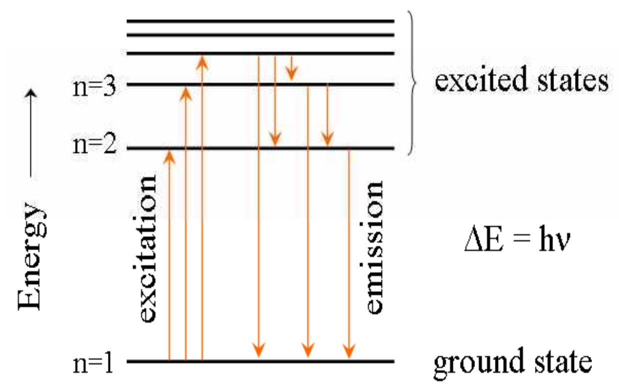


그림 Ⅱ-29 원자의 빛의 흡수와 방출



ICP-AES

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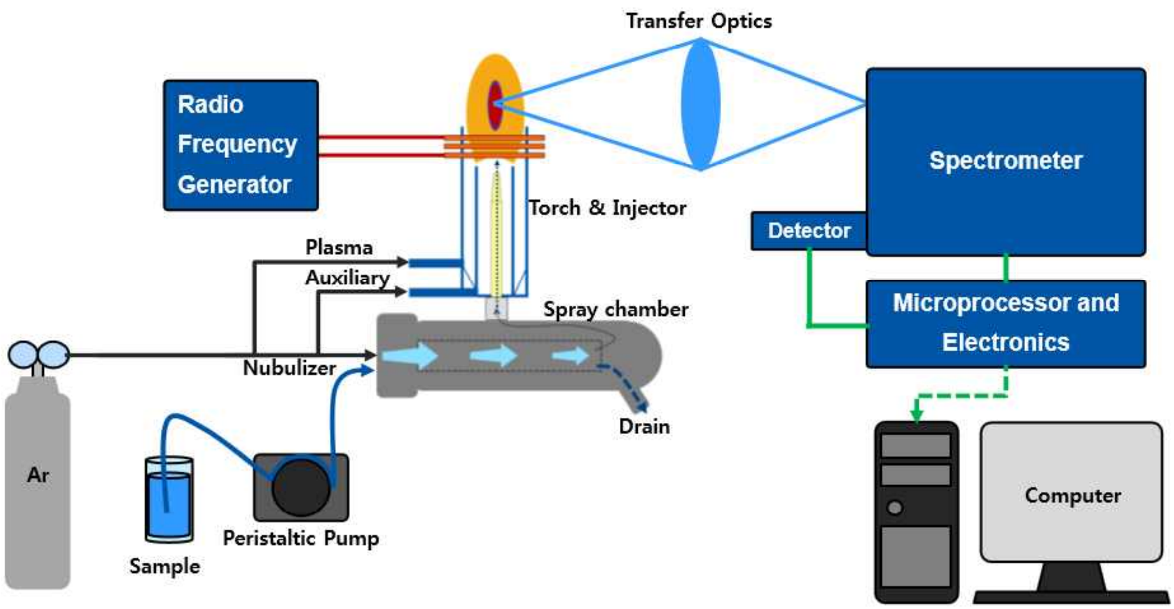
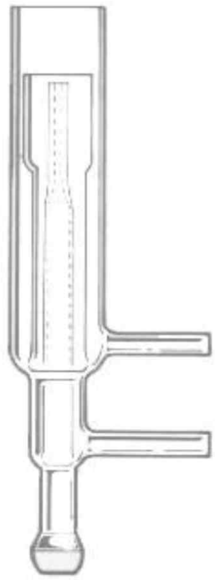
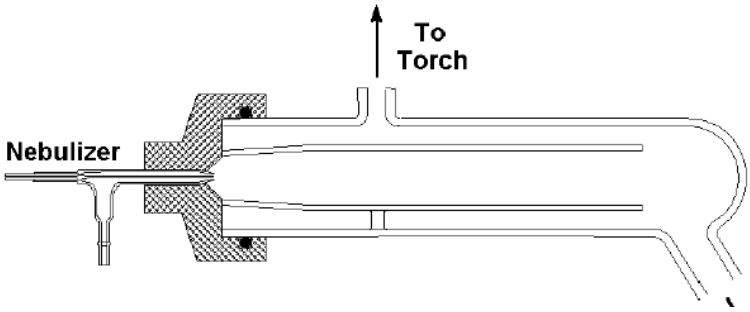
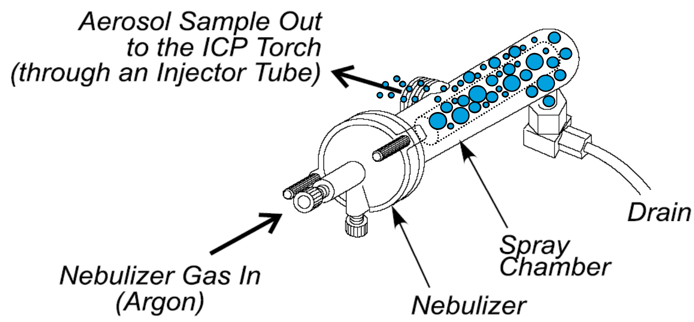


Torch & nebulizer

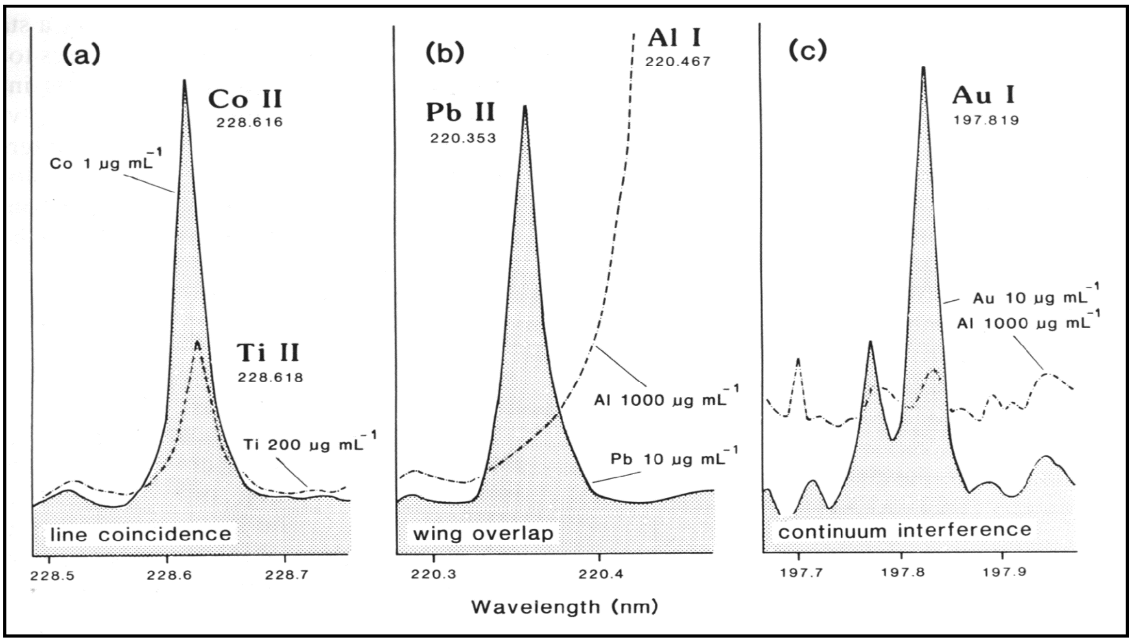






Spectroscopic Information

- **Qualitative**
  - **related to wavelengths at which radiation is emitted or absorbed**
- **Quantitative**
  - **related to amount of radiation emitted or absorbed at analyte wavelength depends on concentration**



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ICP-MS 특징

- Extreme detection capability
  - Opened up detection of ppb and ppt concentration levels
- ICP-MS provides a powerful identification tool
  - Simple spectrum is based on fundamental properties of atoms
- Elements are well resolved - minimal elemental interferences.
- Quantitative analysis benefits from high linearity of detection
  - Wide measurement range (dynamic range)
    - Semi-quantitative analysis provides concentration results without a calibration standard.
- ICPMS readily accommodates add-on attachments
  - Flow injection, Laser ablation, GC, LC, etc.
- Isotope measurement capability has multiple applications
  - Geological, nuclear, biomedical

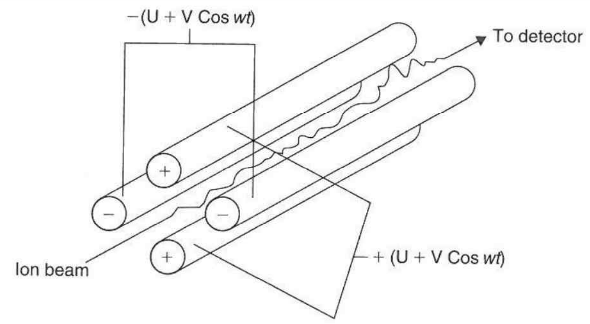
ICP-MS의 원리

- 용액 시료를 분무기, spray chamber, 토오치를 통해 플라즈마에 주입
- 플라즈마 내에서 시료 용매는 증발되고 분자들이 구성 원자로 나뉘어지며 이온화 된다.
- 플라즈마에서 형성된 이온들이 Sample 및 Skimmer Cone을 통해 고진공 지역으로 들어감
- 이온 집중 렌즈는 + 이온들을 집중하여 질량 분석기로 유도
- 질량분석기를 통과한 이온들은 이온증폭 검출기에 의해 검출됨
- 사중극 자 질량분석기 내에서 이온들이

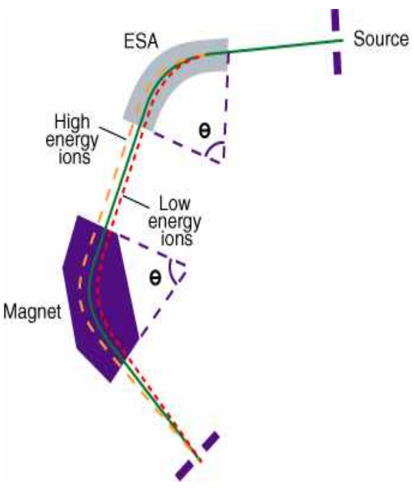
  질량/전하 (m/z) 비율에 따라 분리됨

ICP-MS

- Quadrupole System
- Double Focusing Magnetic Sector System (HR-ICP-MS)
- Time –of –Flight system



Schematic diagram of a quadrupole mass analyser.



Double focusing

ICP-MS

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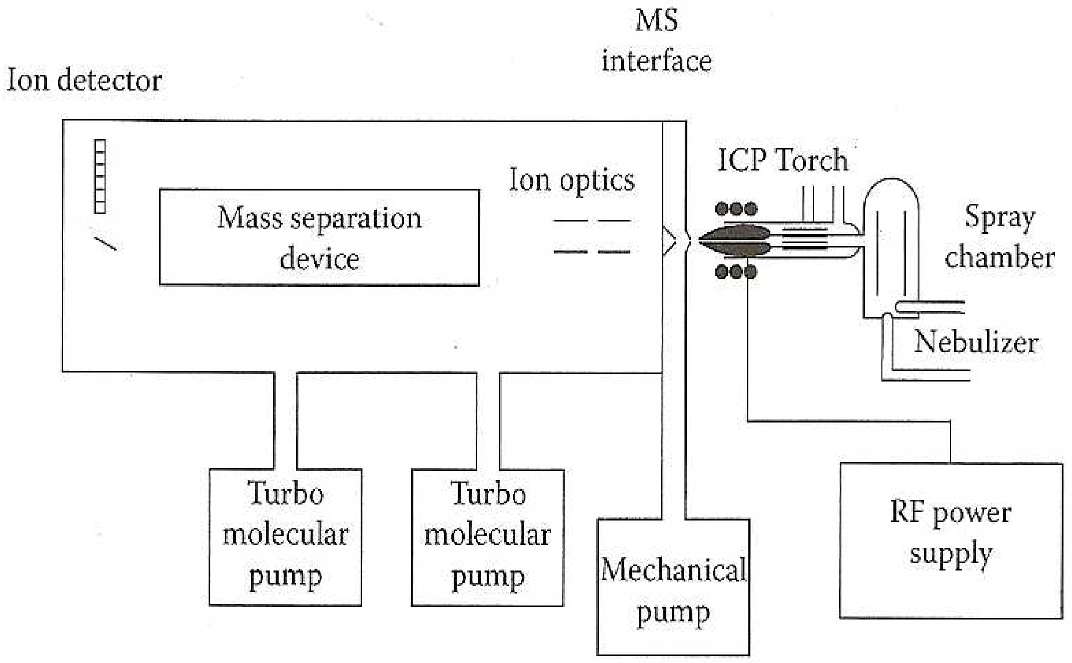

ICP-MS

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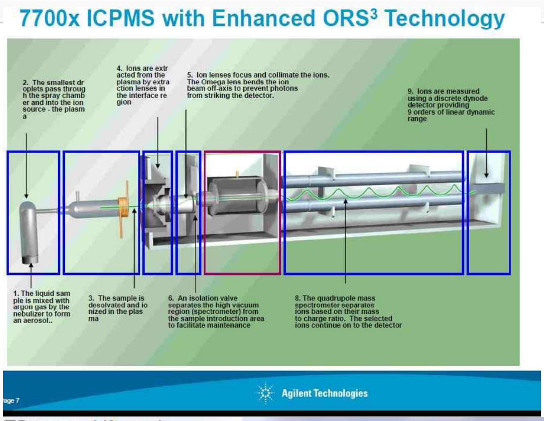


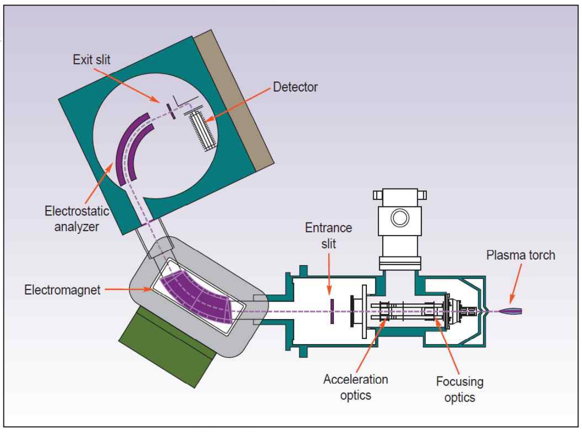


Figure 1. Schematic of a reverse Nier-Johnson double-focusing magnetic-sector mass spectrometer (Courtesy of Thermo Finnigan [San Jose, CA]).

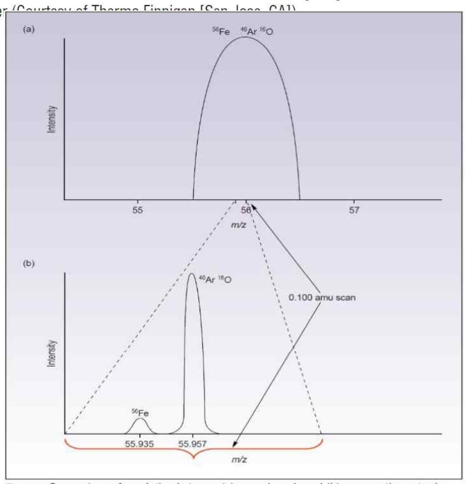
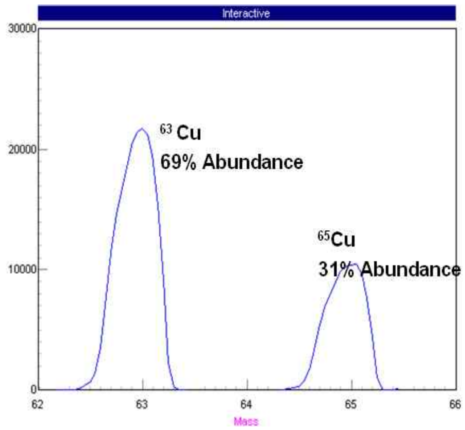


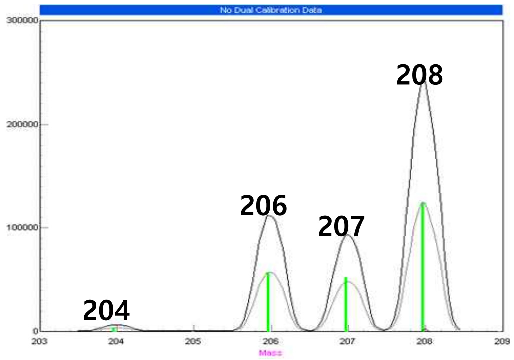
Figure 6. Comparison of resolution between (a) a quadrupole and (b) a magnetic-sector instrument for the polyatomic interference of $^{40}Ar^{16}O$ on ^{56}Fe.

Ion formation

Isotope	Mass	Abundance
Cu 63	62.9298	69.170000
Cu 65	64.9278	30.830000



Isotope	Mass	Abundance
Pb 204	203.9730	1.400000
Pb 206	205.9750	24.100000
Pb 207	206.9760	22.100000
Pb 208	207.9770	52.400000



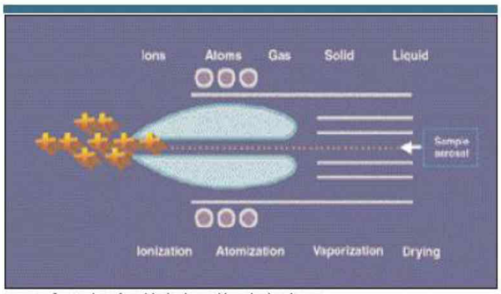


Figure 1. Generation of positively charged ions in the plasma.

Mass Spectrum

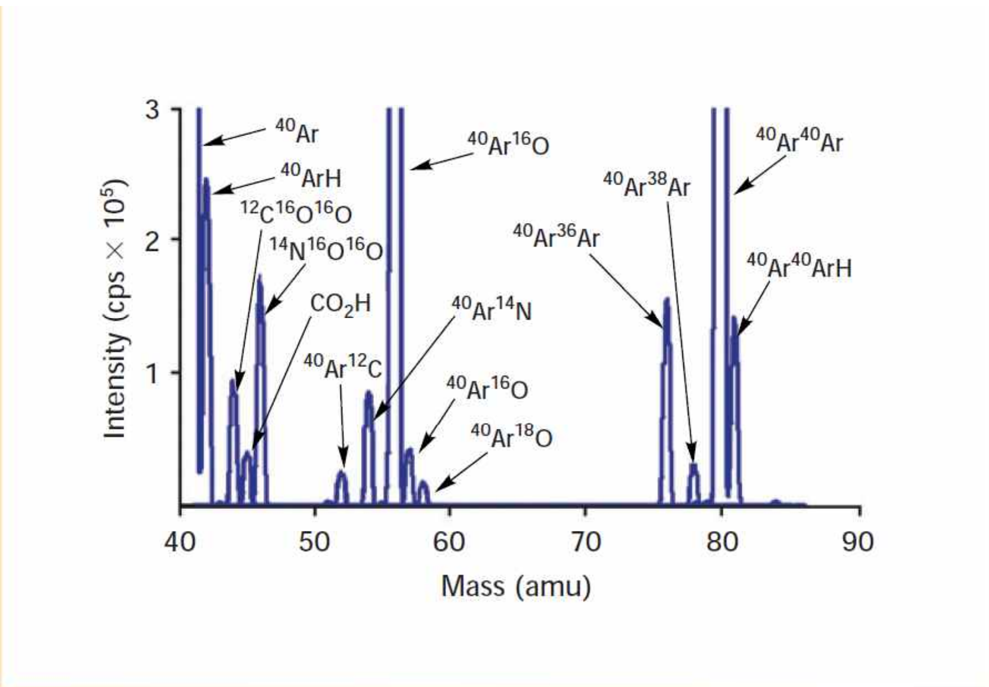


Figure 1. Mass spectrum of deionized water from mass 40 to mass 85.

시료 전처리

Sampling

- Laboratory-sized sample :
  Representative of bulk materials being investigated

시료 전처리 : 시료 용액화

1. 물에 의한 용해
   : 가장 이상적인 전처리 방법 (대부분의 시료는 물에 녹지 않음)

2. 산(Acid)에 의한 분해
   : HCl, HNO_3, HF, $HClO_4$, H_2SO_4, H_2O_2, H_3PO_4등
   : 단일산 , 혼합산, 묽은산, 진한산등을 이용
   : 용해 후 가열하여 산은 날려보냄
   : 다량의 처리가 가능
   : 산을 가하는 방법 중 가장 단순한 방법
   : 시약과 시료를 가하기 쉽다

Air particulate

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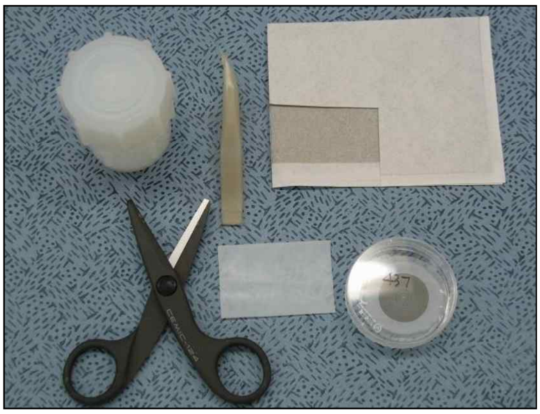

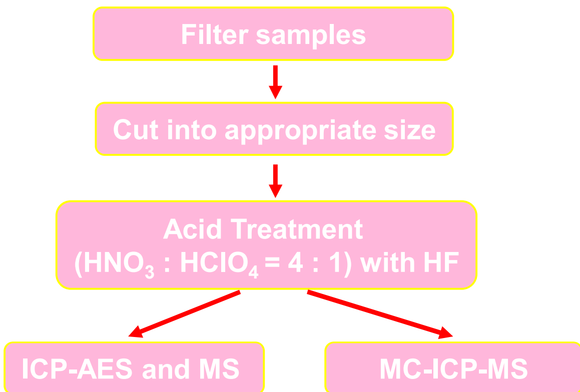

- ICP-AES : Al, Fe, Mn, Ca, Mg, K, V, Ti, Cr, Zn, Cu
- ICP-MS : Trace (V, Ti, Cr, Zn, Cu, 포함), 희토류원소 (REE)
- MC-ICP-MS : 동위원소비율측정 (^{206}Pb, ^{207}Pb, ^{208}Pb)
- SRM : (NIST 2783, Air particulate on Filter Media)
- Spike에 의한 회수율측정

Wet digestion in open & closed system

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Open system

- Effective on both inorganic and organic materials
- Large sampling
- Simple and economic
- Longer digestion time
- Contamination caused by reagents and vessels
- Losses of element caused by adsorption and by reaction with vessel
- Losses of elements by volatilization

Closed system

- No volatilization losses of elements
- Shorter reaction time
- Improved decomposition
- Bank values are decreased because of reduced reagent quantities
- No contamination from external source

전처리 용기 (Reflux형)

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Microwave digestion System

- Mostly use 2450 MHz
- Coupling of electromagnetic radiation with acids
- Speed up the dissolution : rapid heating ability of microwave
- No contamination from environment
- Automation
- No volatilization loss
- expensive

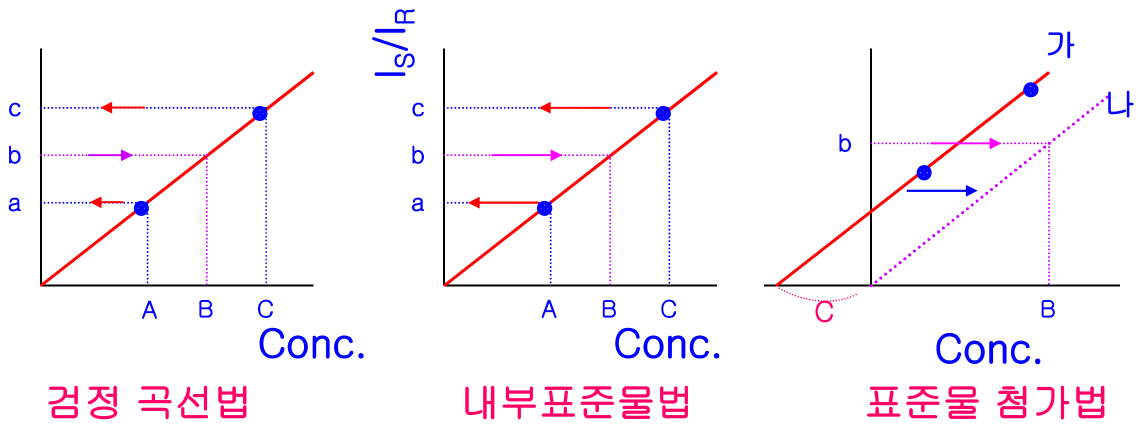
- Dilution factor,
- Acidity ⇒ hotplate에서 재처리
- Vessel cleaning

Procedure for ICP-MS Measurement

SAMPLE NAME	LIMITS	COMMENTS
Tuning		Instrument setup
Calibration standards	Blank	4 points (blank 포함)
	STD I	0.1 ppb
	STDⅡ	1.0 ppb
	STDⅢ	10.0 ppb
Continuing Calibration Blank (CCB)		1 % HNO_3
Initial Calibration Verification (ICV)	%REC 90-110	Source different from calibration
Laboratory Control Sample (LCS)	%REC 80-120	CRM
Batch Ⅰ		
Sample preparation blank CRM (digested with samples)		1 % HNO_3
Sample 1		
Sample 1 - Duplicate	%REC 90-110	
Sample 2 ~ Sample 25		
Continuing Calibration Verification (CCV)	%REC 90-110	Calibration standard - STDII
Batch Ⅱ		
Sample 25		
Sample 25 - Duplicate	%REC 90-110	
Sample 26 ~ Sample 50		
CRM (digested with samples)		
Continuing Calibration Verification (CCV)	%REC 90-110	Calibration standard - STDII

시료 정량법

1). 검정곡선법 (Calibration method)
2). 내부표준물법(Internal standard method)
3). 표준물첨가법(Standard addition method)



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$$A = \frac{\text{전처리한 시료량(mL or g) X 측정 농도(ng/mL or ng/g) X 면적비}}{\text{유량}(m^3)}$$

ex) 시료를 전 처리하여 20.00 g을 만들어 Cu를 ICP-MS 를 측정했을 때 측정 값이 50.00 ng/g 였을때 공기 중 Cu 의 농도 계산

단, 사용한 필터 크기 : 4 cm * 6 cm (18 cm * 23 cm), 유량 48 m^3

$$\text{Cu농도} = \frac{20.00\ g\ X\ 50.00\ ng/g\ X\ 17.25}{48.00(m^3)} = 359\ ng/m^3 = 0.36\ \mu g/m^3$$

Schematic Diagram of double focusing MC-ICPMS

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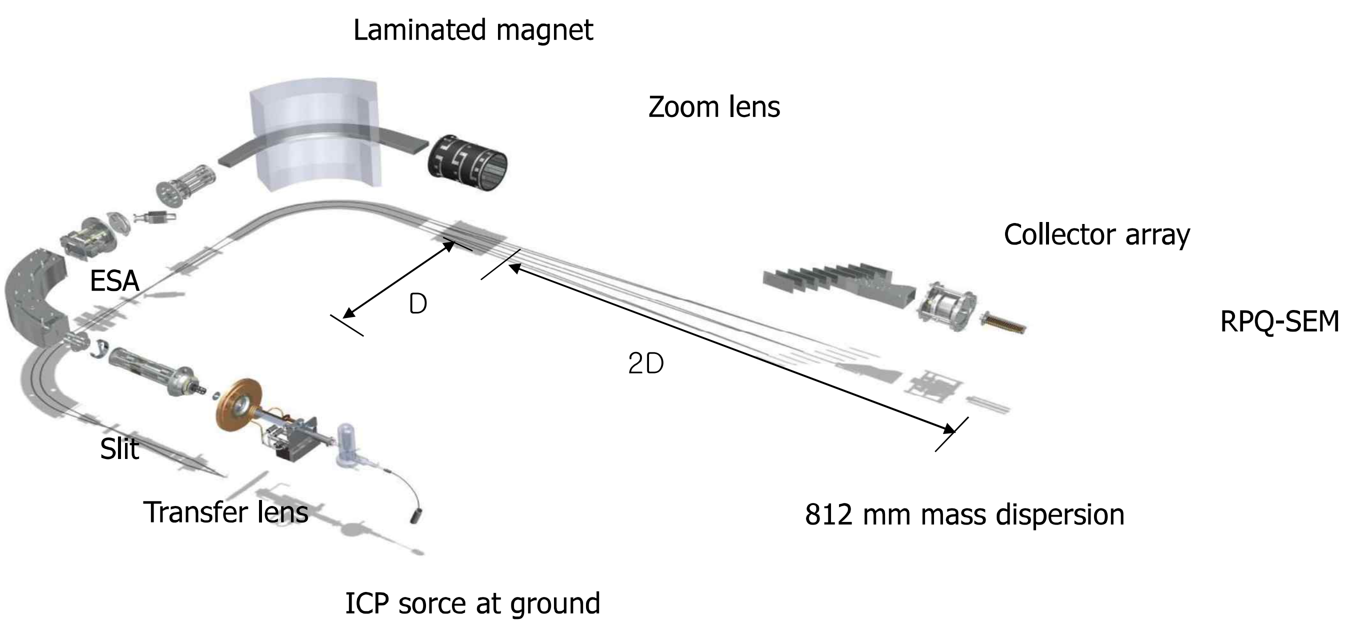

From Thermo Electron Co.

Principles of MC-ICP-MS

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- **Ions are accelerated to high (6-10 kV) energy**
- **High precision transfer optics focuses the ion beam**
- **Double focusing mass spectrometer reduces ion energy spread and separates the ions according to their mass to charge ratio**
  - **ESA = Energy filter**
  - **Magnet = Mass filter**
- **Pseudo or High resolution is achieved by varying source and collector slit**
- **Ions are collected by detector system**
  - **Discrete Dynode Electron Multiplier**

Characteristics of MC-ICP-MS

1. High Precision of Isotopic Results

   농도 분석 , Pb = (20 ± 2)mg

   동위원소비율 $^{206}Pb/^{204}Pb$ = 20.000 ± 0.001

2. Direct sample solution introduction

Fast sample turn-around, Less labour intensive than TIMS

3. Faster sample throughput

MC-ICP-MS에서 사용되는 주요 원소

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✓ Lithium (Li):

Two stable isotopes (^{6}Li & ^{7}Li) with the significant relative mass difference (~ 16%)
Natural mass fractionation: ~ 6% variation among geological materials
Broad elemental dispersion in Earth and planetary materials

✓ Magnesium (Mg):

The second in abundance among the rock-forming elements
Three stable isotopes with the large relative mass difference (4 and 8% between ^{25}Mg & ^{26}Mg, and ^{24}Mg, respectively)
Necessary resolution: better than 200 ppm
Reproducibility of 30 to 60 ppm or better during a last decade

✓ Plutonium (Pu):

Widely regarded as a man-made element with five isotopes
The two most abundant Pu isotopes (^{239}Pu & ^{240}Pu) reveal the characteristic of contamination sourceS

✓ Uranium (U):

Three naturally occurring isotopes (^{234}U, ^{235}U & ^{238}U)
Important radiogenic isotope in geochronology and geochemistry for the evolution of Earth

1. **Li, Mg** : 지하수, 해수, 암석등 지질시료의
   지구화학 과정의 지시자:동위원소 분별기작,풍화 과정 중 원소 순환
2. **Pb** : 분진,토양 및 퇴적물 시료의 오염원 및 기원지 추적자로 사용
3. **Sr** : 원산지 판별 추적자 (배추, 인삼...)
   수질 시료의 지구화학적 기원추적

KBSI 원소분석실

1. ICP-AES(2) : OPTIMA 8300
2. ICP-MS (2) : X5, X2
3. HR-ICP-MS : AttoM
4. LA-ICP-MS : 193 nm & iCAP
5. MC-ICP-MS : Neptune
6. MC-ICP-MS : Sapphire
7. ICP-TQ-MS
8. Mercury Analyser
9. Ion Chromatography

과학으로 지키는 국민행복, with KBSI!

Thank You

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안정동위원소 기기 활용 (EA-IRMS 관련, 원산지 판별)

봉연식 (한국기초과학지원연구원)

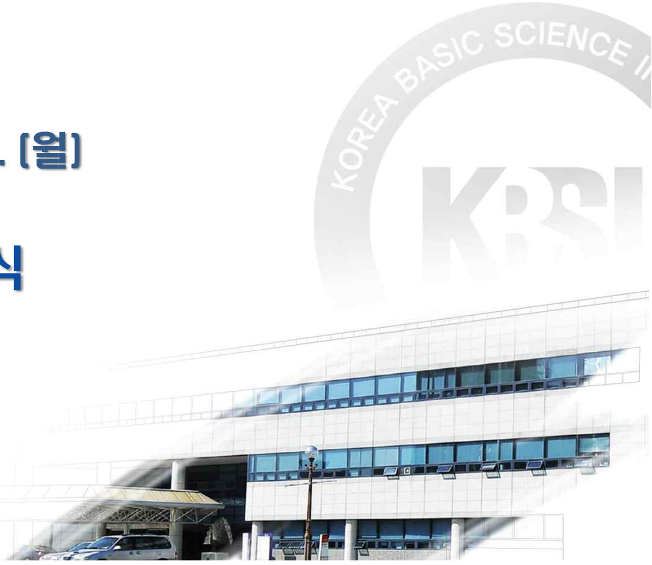
서해안기후환경연구소
세미나

안정동위원소 기기 활용

EA-IRMS 관련, 원산지 판별

2020. 2. 24. (월)

봉 연 식



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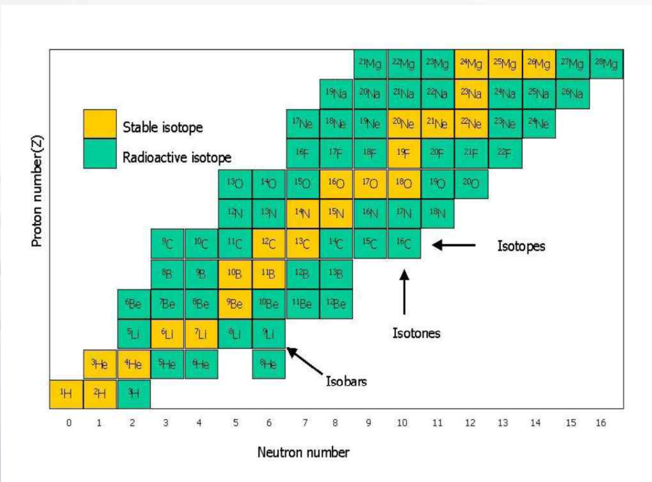
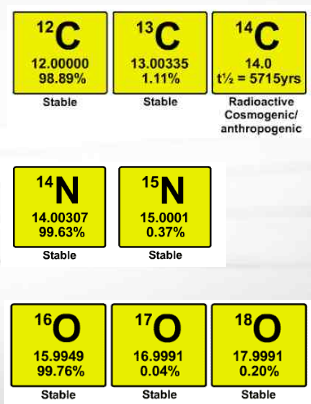
동위원소 지구화학

동위원소(同位元素, ISOTOPE)

mass number (A) → 12, atomic number (Z) → 6: $^{12}_{6}C$

- 희랍어의 isos(equal) topos(site, place)에서 유래
- 동일한 화학원소 중에서 질량이 다른 원소
- 원자번호(양자수)는 같지만, 중성자수가 다르기 때문에 질량이 다른 원소
- 화학적 성질은 같지만 물리적 성질이 다름
- 자연에는 현재 약 339핵종이 알려져 있으며, 그 중 74%(250종)가 안정동위원소





안정동위원소 지구화학

안정동위원소의 표현법

- 안정동위원소 : 상대적인 차이(Relative Difference)
  - 비교되는 두 원소간의 질량 차가 적고 분석하고자 하는 시료의 종류, 준비과정, 분석기 등의 영향으로 동위원소의 절대량을 측정하는 것이 어려움
  - 시료의 동위원소 비 (R_{sample})와, 표준시료의 동위원소 비 ($R_{standard}$)를 천분율 (‰) 편차로 나타내고, 델타 (δ)로 표기

$$ratio\ (R) = \frac{abundance\ of\ the\ heavy\ isotope}{abundance\ of\ the\ light\ isotope}$$

R = D/H, $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$, $^{34}S/^{32}S$

$$\delta(‰) = (\frac{R_{sample}}{R_{standard}} - 1) \times 1000$$

Standard = V-SMOW, V-PDB, V-CDT, AIR

$$\delta^{13}C_{VPDB}\ (‰) = (\frac{^{13}C/^{12}C_{sample}}{^{13}C/^{12}C_{standard}} - 1) \times 1000$$

안정동위원소 지구화학

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안정동위원소의 종류

Abundance of Commonly Used Stable Isotopes:

^{1}H (99.9844%), ^{2}H (D, 0.0156%)

^{12}C (98.89 %), ^{13}C (1.11 %)

^{14}N (99.64%), ^{15}N (0.36%)

^{16}O (99.76%), ^{17}O (0.0375%), ^{18}O (0.2%)

^{32}S (94.93%), ^{33}S (0.76%), ^{34}S (4.29%), ^{36}S (0.02%)

▣ 유용한 안정동위원소 지시자의 조건:

- 동위원소 간 질량차이가 클 것
- 다양한 존재 형태(고체, 액체, 기체)를 가질 것
- 많이 존재하고 다양한 물질에 포함될 것, 등

안정동위원소 질량분석기

질량분석기의 구조

› 주요 구성요소 : Inlet, Ion Source, Magnet, Detector

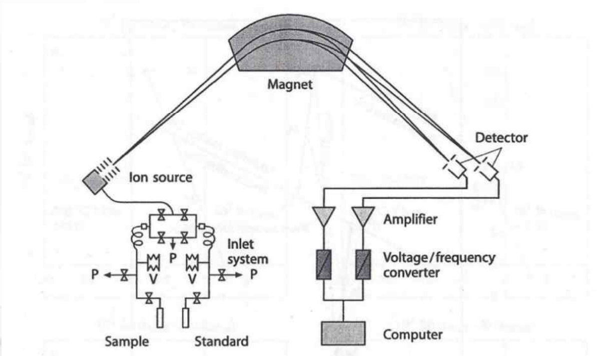
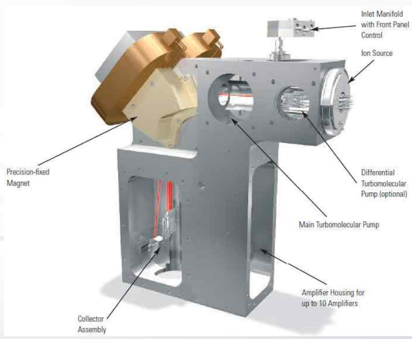


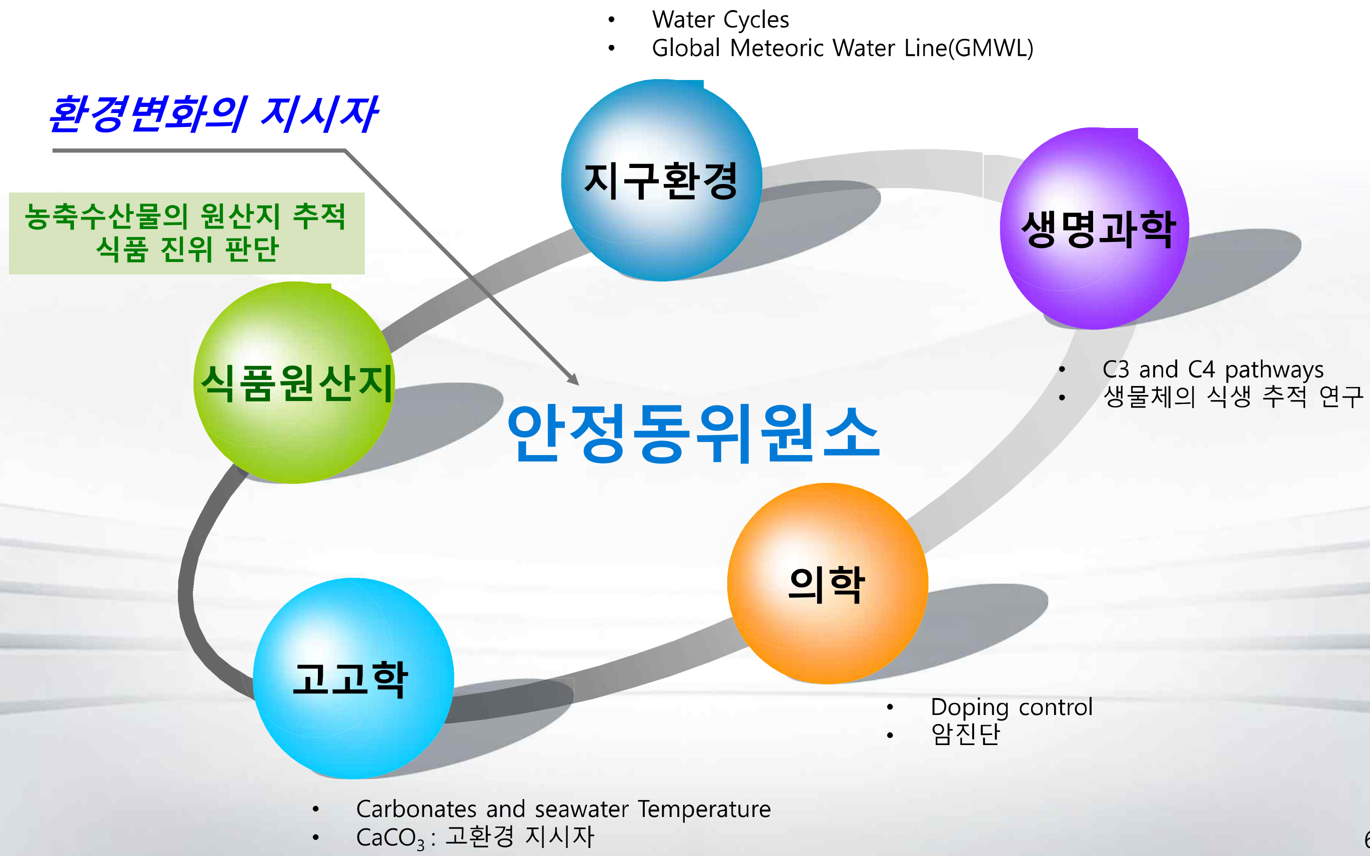
Fig. 1.8 Schematic representation of a gas-source mass spectrometer for stable isotope measurements. P denotes pumping system, V denotes a variable volume

Hoefs J., 2009. *Stable Isotope Geochemistry*. 6th ed., Springer

□ 안정동위원소 분석: 주로 가스용 질량분석기 (gas source mass spectrometer)
• 기체시료 이외의 모든 고체 물질 또는 액체 시료는 가스화 하여야 함.
• 많은 경우 진공장치 내에서 화학적 처리나 연소 등의 과정에서 시료를 가스화하여 전처리 함.
• 과거에는 많은 경우 오프라인에서 시료를 준비하였으나, 최근에는 온라인 시스템으로 원소분석 장치에서 질량분석장치로 직접 연결해 질량분석을 실시.



안정동위원소의 활용



동위원소 지시자

Isotope ratio	Fractionation	Information
$^{2}H/^{1}H$	evaporation, condensation, precipitation	geographical
$^{13}C/^{12}C$	C_3 and C_4 plants	diet (geographical proxy)
$^{15}N/^{14}N$	trophic level, marine and terrestrial plants, agricultural practice	diet (geographical proxy)
$^{18}O/^{16}O$	evaporation, condensation, precipitation	geographical
$^{34}S/^{32}S$	bacterial	geographical (marine)

Kelly et al., (2005) Trends in Food Science & Technology

- Pink box → Indicators of climatic conditions
- Purple box → Depend on local agricultural practices and animal diets
- Green box → Indicators of geology

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원산지 판별에 이용되는 동위원소 지시자

Stable isotopes: a powerful authentication tool

eurofins

The content of...	Is influenced by…	And can reveal…	Examples
^{13}C, ^{2}H	Botanical origin	Addition of sugars from other plants	Fruit juices
^{13}C, ^{2}H	Synthetic pathway	Addition of artificial substances	Flavours : vanillin...
^{18}O, ^{2}H	Origin of water	Dilution with tap water	Wines, NFC juices
^{13}C, ^{18}O, ^{15}N ^{2}H, etc.	Geographic origin	Mislabeling of origin	All products
^{13}C, ^{15}N	Diet	Feeding regime	Animal products

한국기초과학지원연구원

지구환경연구부

한국기초과학지원연구원/지구환경연구부

지구환경 동위원소, 미량원소, 방사능 분야 분석 및 연구

- Isotope measurement
- Trace element measurement
- Radioactivity measurement
- Quaternary dating

Core facility of earth & environmental research in Korea

- Geological age determination
- Climate change
- National agenda
  - food origin
  - forensic science
- Archeological & anthropological application

동위원소 분석 기기

국내 최고 수준의 장비와 인력

유기물 탄소/질소/황 동위원소 측정 장비: EA-IRMS

유기물 산소/수소 동위원소 측정 장비: HT/EA-IRMS

물 산소/수소 동위원소 측정 장비: EA-IRMS

스트론튬 동위원소 측정 장비: MC-ICP-MS

안정동위원소 질량분석기

원소분석기(EA)

질량분석기(IRMS)

- 모델명: IRMS, Isoprime
- 취득일자: 2005년
- 구 성:
  - IRMS
  - EA
- 주 이용분야:
  - 고체시료 탄소, 질소 동위원소 분석

✓ *불용처리: 2016년*

안정동위원소 질량분석기

원소분석기(EA)

질량분석기(IRMS)

- 모델명: Isoprime 100
- 취득일자: 2015년
- 구 성:
  - IRMS
  - GC, Interface
  - Pyr cube EA

- 주 이용분야:
  - 성분별 탄소 동위원소 분석
  - 고체 탄소, 질소, 황, 산소, 수소 동위원소 분석

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안정동위원소 질량분석기

- 모델명: Isoprime 100
- 취득일자: 2009년
- 구 성:
  - IRMS
  - Multiprep
  - Dual Inlet
  - PyrOH EA, Auto Sampler
  - HT/EA

- 주 이용분야:
  - 물 산소 동위원소 분석
  - 물 수소 동위원소 분석
  - 탄산염 시료의 탄소, 산소 동위원소 분석
  - CO_2가스의 탄소 동위원소 분석
  - 고체 산소, 수소 동위원소 분석

안정동위원소 질량분석기

- 모델명: Delta V Plus
- 취득일자: 2013년
- 구 성:
  - IRMS
  - H/Device
  - GasBench II

- 주 이용분야:
  - 물 산소, 탄소 동위원소 분석
  - 물 수소 동위원소 분석
  - 탄산염 시료의 탄소, 산소 동위원소 분석
  - CO_2가스의 탄소 동위원소 분석

안정동위원소 질량분석기

- 모델명: Vision
- 취득일자: 2017년
- 구 성
  - IRMS
  - Pyr cube EA

- 현재 이용
- **고체 탄소, 질소, 황 동위원소 분석**
- 농산물 시료의 안정동위원소 분석

안정동위원소 질량분석기

원소분석기(EA)

Conflo

질량분석기(IRMS)

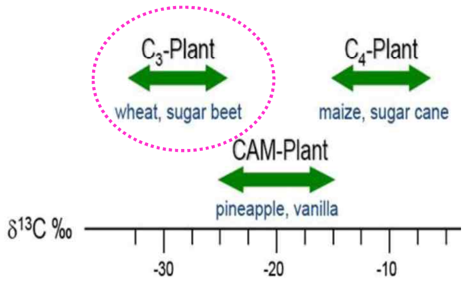
원소분석기(EA):
HT/EA

- 모델명: Delta Advantage
- 취득일자: 2013년
- 구 성:
  - IRMS
  - Conflo
  - EA
  - HT/EA

- 주 이용분야:
  - 고체 탄소, 질소, **산소, 수소 동위원소 분석**

탄소동위원소를 이용한 과일농축액 및 벌꿀 진위여부 판별

탄소 동위원소 측정 장비: EA-IRMS



기기분석

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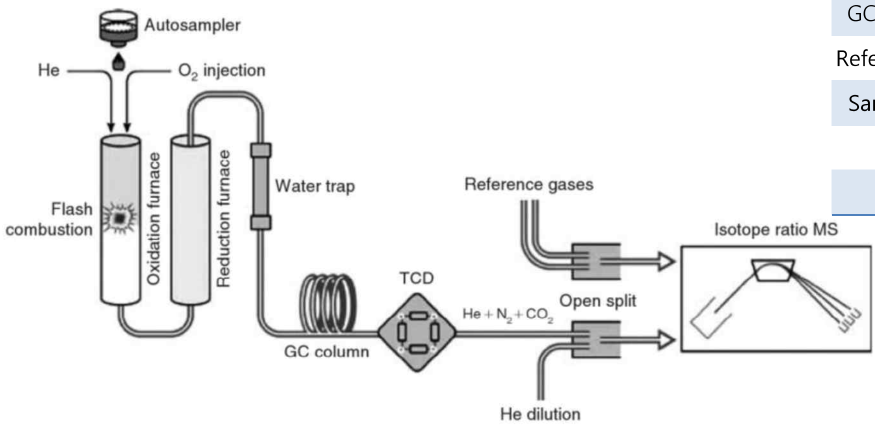
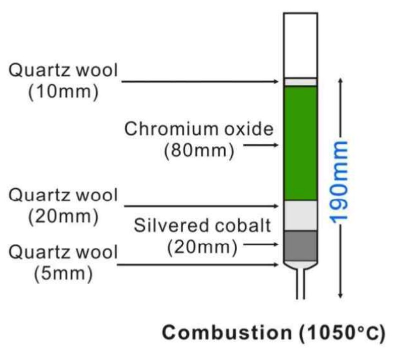
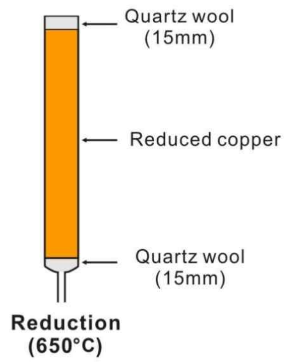
Elemental-analyzer(EA)-IRMS system



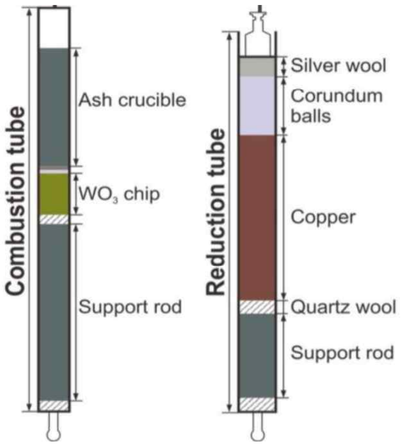
Parameters	Operating conditions
Combustion furnace	1,050 ℃
Reduction furnace	650 ℃
GC packed column oven	115 ℃
Reference capillary column	L=1.5 m, I.D.(f)=100 mm
Sample capillary column	L=2.5 m, I.D.(f)=75 mm
Run time	385 sec
He carrier flow	115 ml/min



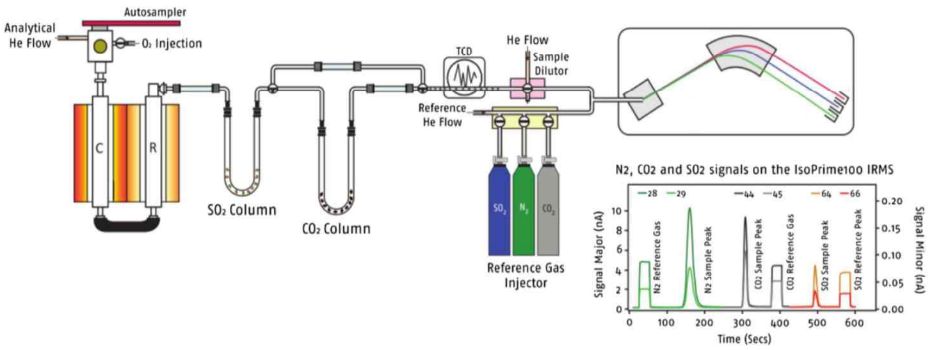


- Elemental-analyzer(EA)-IRMS system

Parameters	Operating conditions
Combustion furnace	1,150 ℃
Reduction furnace	850 ℃
O_2 dosing time	120 sec
CO_2 desorption	110 ℃
Run time	600 sec
He carrier flow	220 ml/min



(Kim et al., 2017)



(Agnihotri et al., 2014)

- EA-IRMS를 이용한 유기물 **탄소** 분석에 이용되는 표준물질

Standard material	$\delta^{13}C_{VPDB}$ (‰)
IAEA-600, Caffeine	-27.771
IAEA-CH-6, Sucrose ANU	-10.449
NBS 22, Oil	-30.031
USGS 40, L-Glutamic acid	-26.389
IAEA-CH-3, Cellulose	-24.724
UREA (KBSI-lab standard)	-36.46
urea (KBSI-lab standard)	-8.02

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시료준비
- 시료 상태 확인(균질화 정도)
- Tin capsule에 시료 담기(무게측정)

원소분석기 안정화
- Combustion tube, reduction tube 충진 상태 확인
- Carrier gas (He) leak test, reference gas (CO_2), O_2 gas 상태 확인
- Combustion furnace(1050℃), reduction furnace(650℃), GC column oven(115℃) 온도 설정

질량분석기 안정화
- Reference gas beam size 확인
- Peak center 실행
- Reference gas stability test (reference peak 동위원소 비의 표준편차 확인)

시료 분석
- 시료 특성에 따라 표준물질 선정
- Calibration standard

결과 보정
- 시료 양과 측정된 동위원소 비의 상관관계식 만들기
- 국제 표준물질을 이용한 standard curve 만들기

기기분석

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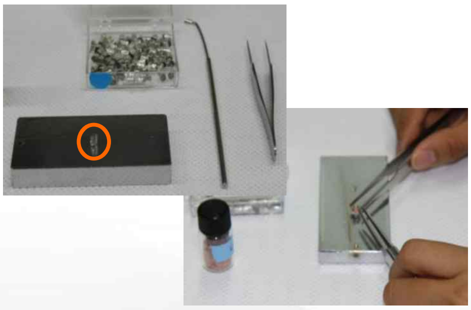
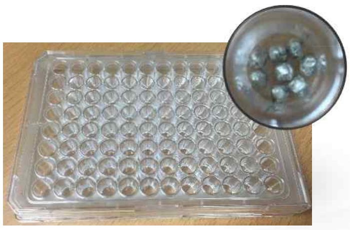
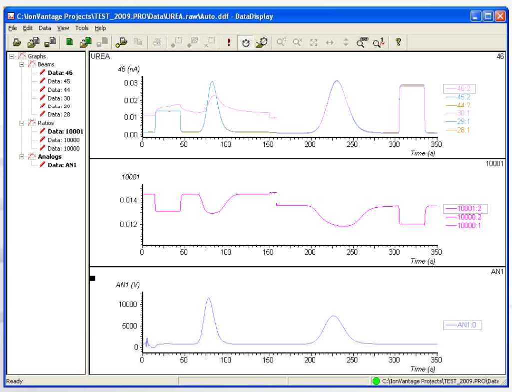
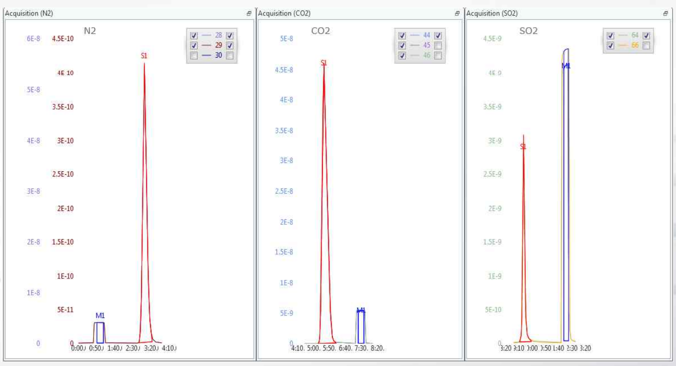



분석할 시료와 표준물질 tin capsule에 담기

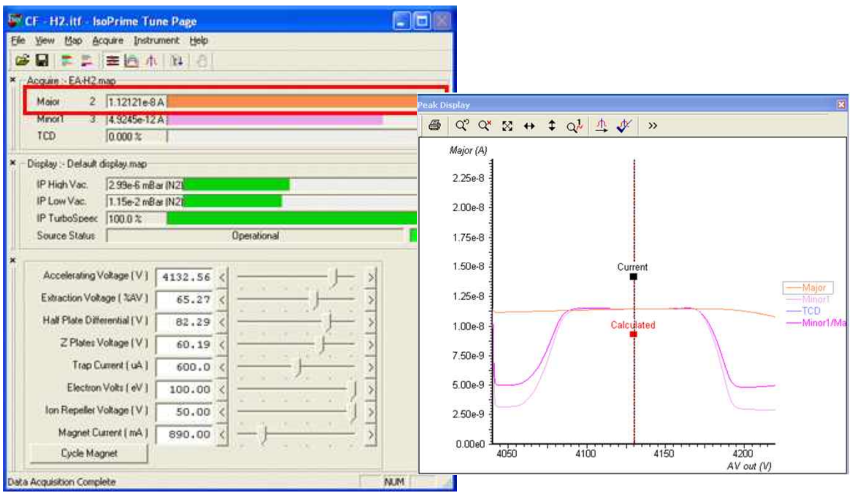
Auto sampler에 시료 loading

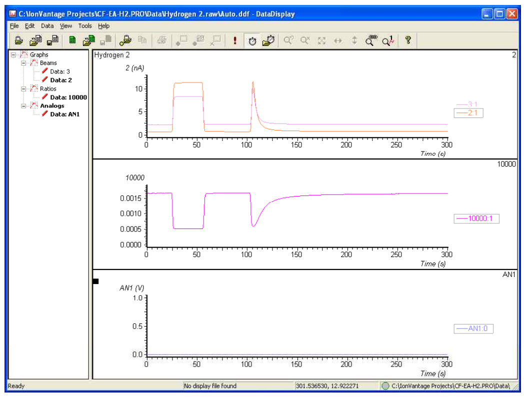


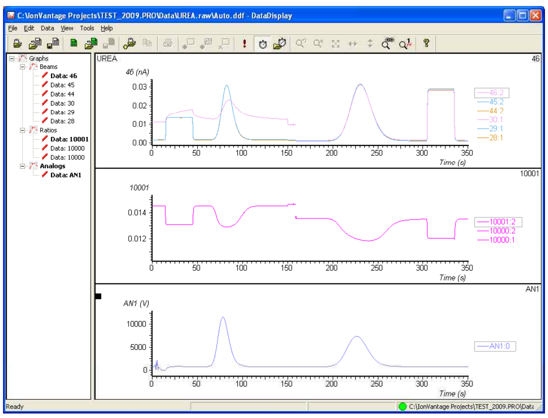
EA-IRMS를 이용한 분석

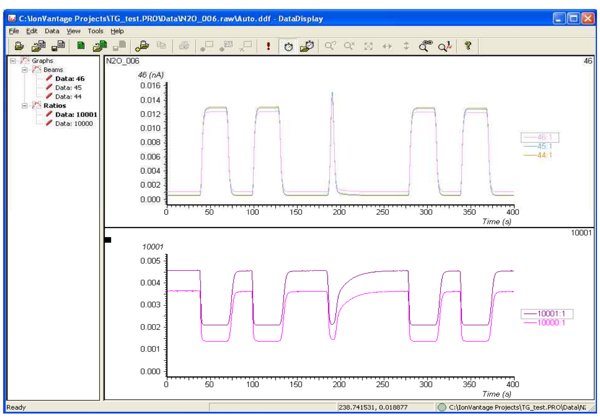


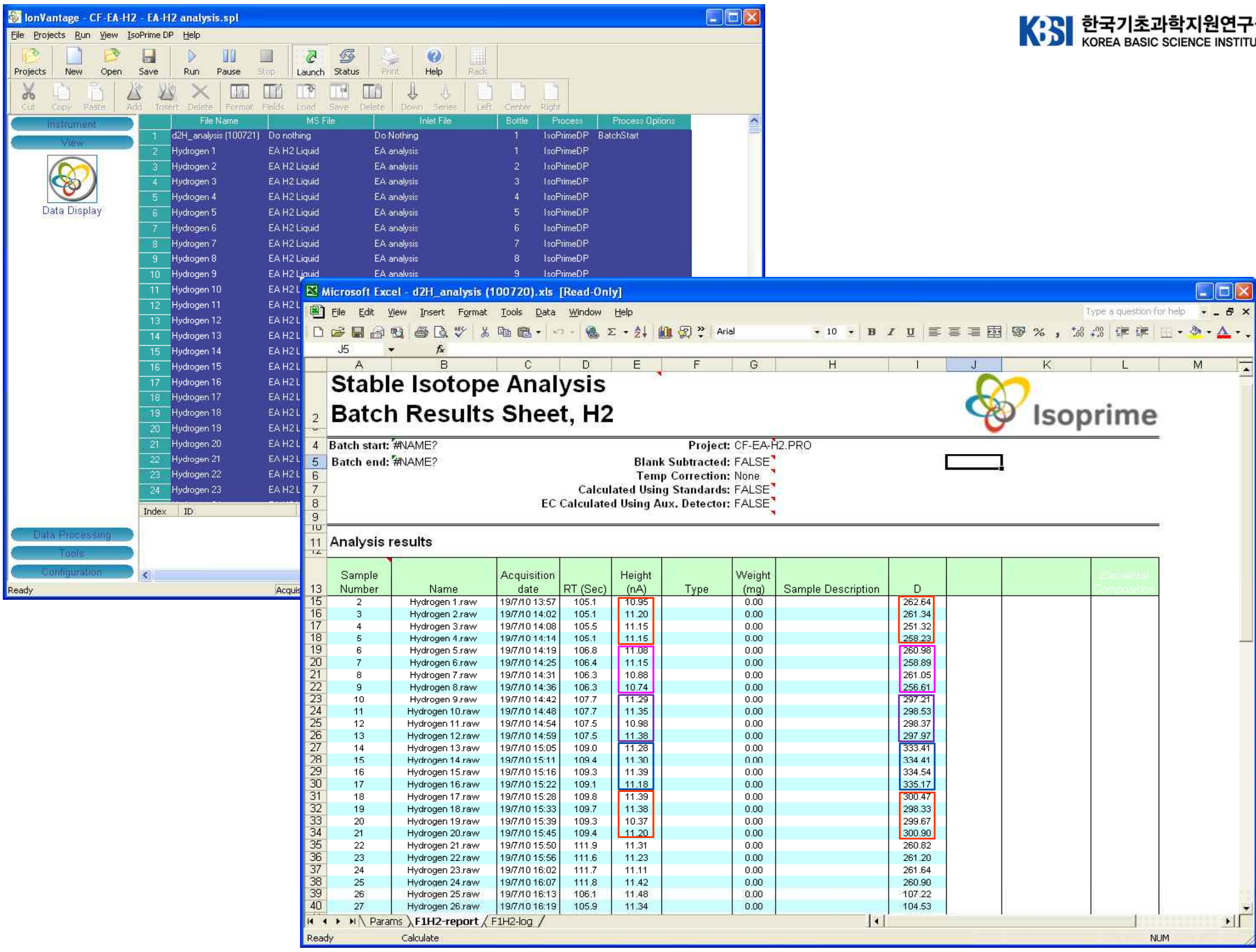
질소_N_2 탄소_CO_2 황_SO_2


CF - H2.itf - IsoPrime Tune Page
File View Map Acquire Instrument Help
Acquire :- EA-H2 map
Major 2 1.12121e-8 A
Minor1 3 4.3245e-12 A
TCD 0.000 %
Display :- Default display map
IP High Vac. 2.99e-6 mBar (N2)
IP Low Vac. 1.15e-2 mBar (N2)
IP TurboSpeed 100.0 %
Source Status Operational
Accelerating Voltage (V) 4132.56
Extraction Voltage (%AV) 65.27
Half Plate Differential (V) 82.29
Z Plates Voltage (V) 60.19
Trap Current (uA) 600.0
Electron Volts (eV) 100.00
Ion Repeller Voltage (V) 50.00
Magnet Current (mA) 890.00
Cycle Magnet
Data Acquisition Complete
NUM
Peak Display
Major (A)
Current
Calculated
Major
Minor1
TCD
AV out (V)


Hydrogen 2
Time (s)


UREA
Time (s)


N2O_006
Time (s)



Sample Number	Name	Acquisition date	RT (Sec)	Height (nA)	Type	Weight (mg)	Sample Description	D
2	Hydrogen 1.raw	19/7/10 13:57	105.1	10.95		0.00		262.64
3	Hydrogen 2.raw	19/7/10 14:02	105.1	11.20		0.00		261.34
4	Hydrogen 3.raw	19/7/10 14:08	105.5	11.15		0.00		251.32
5	Hydrogen 4.raw	19/7/10 14:14	105.1	11.15		0.00		258.23
6	Hydrogen 5.raw	19/7/10 14:19	106.8	11.08		0.00		260.98
7	Hydrogen 6.raw	19/7/10 14:25	106.4	11.15		0.00		258.89
8	Hydrogen 7.raw	19/7/10 14:31	106.3	10.88		0.00		261.05
9	Hydrogen 8.raw	19/7/10 14:36	106.3	10.74		0.00		256.61
10	Hydrogen 9.raw	19/7/10 14:42	107.7	11.29		0.00		297.21
11	Hydrogen 10.raw	19/7/10 14:48	107.7	11.35		0.00		298.53
12	Hydrogen 11.raw	19/7/10 14:54	107.5	10.98		0.00		298.37
13	Hydrogen 12.raw	19/7/10 14:59	107.5	11.38		0.00		297.97
14	Hydrogen 13.raw	19/7/10 15:05	109.0	11.28		0.00		333.41
15	Hydrogen 14.raw	19/7/10 15:11	109.4	11.30		0.00		334.41
16	Hydrogen 15.raw	19/7/10 15:16	109.3	11.39		0.00		334.54
17	Hydrogen 16.raw	19/7/10 15:22	109.1	11.18		0.00		335.17
18	Hydrogen 17.raw	19/7/10 15:28	109.8	11.39		0.00		300.47
19	Hydrogen 18.raw	19/7/10 15:33	109.7	11.38		0.00		298.33
20	Hydrogen 19.raw	19/7/10 15:39	109.3	10.37		0.00		299.67
21	Hydrogen 20.raw	19/7/10 15:45	109.4	11.20		0.00		300.90
22	Hydrogen 21.raw	19/7/10 15:50	111.9	11.31		0.00		260.82
23	Hydrogen 22.raw	19/7/10 15:56	111.6	11.23		0.00		261.20
24	Hydrogen 23.raw	19/7/10 16:02	111.7	11.11		0.00		261.64
25	Hydrogen 24.raw	19/7/10 16:07	111.8	11.42		0.00		260.90
26	Hydrogen 25.raw	19/7/10 16:13	106.1	11.48		0.00		107.22
27	Hydrogen 26.raw	19/7/10 16:19	105.9	11.34		0.00		104.53

결과보정

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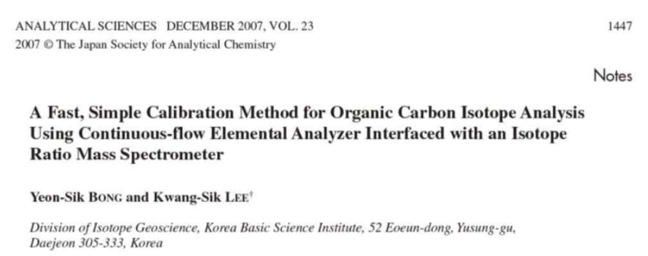
시료 양과 측정된 동위원소 비의 상관관계를 이용한 보정 법



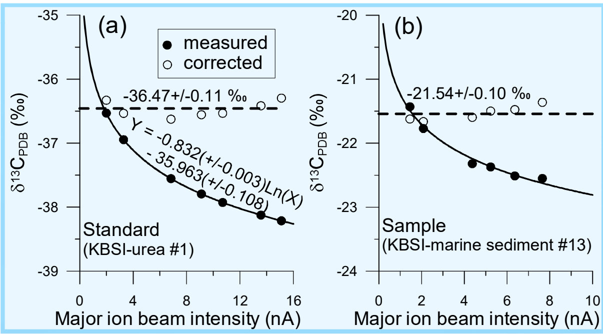
ANALYTICAL SCIENCES DECEMBER 2007, VOL. 23 1447
2007 © The Japan Society for Analytical Chemistry

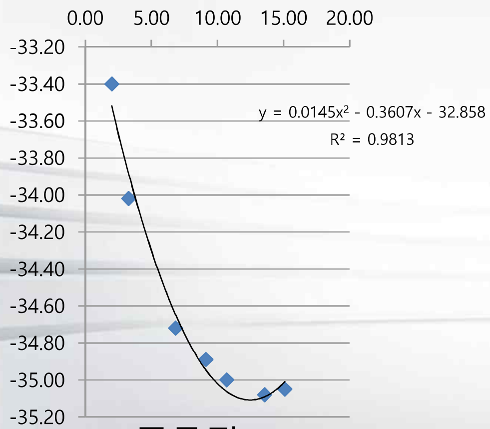
Notes

A Fast, Simple Calibration Method for Organic Carbon Isotope Analysis Using Continuous-flow Elemental Analyzer Interfaced with an Isotope Ratio Mass Spectrometer

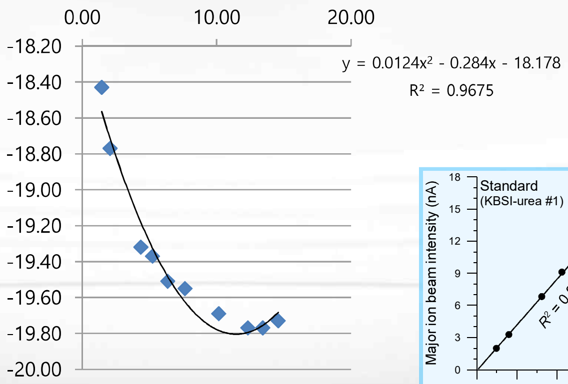
Yeon-Sik BONG and Kwang-Sik LEE†

Division of Isotope Geoscience, Korea Basic Science Institute, 52 Eoeun-dong, Yusung-gu, Daejeon 305-333, Korea

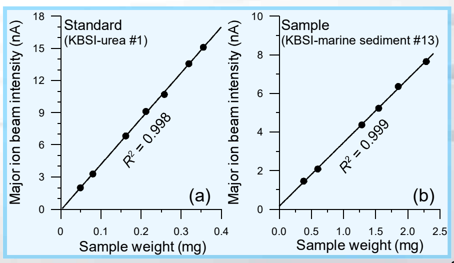




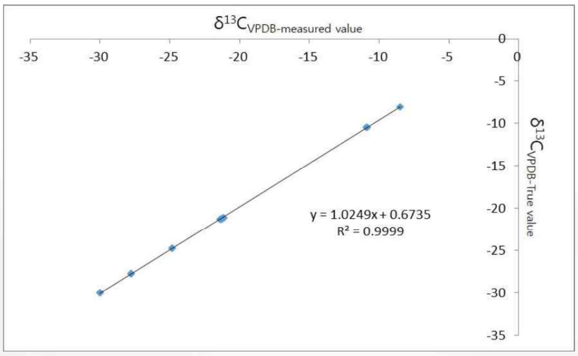
표준물질(UREA)



시료물질(sample)



결과보정



표준물질을 이용한 동위원소 비 보정

동위원소를 활용한 식품원산지 판별

원산지 추적 및 진위 판별 관련 논문

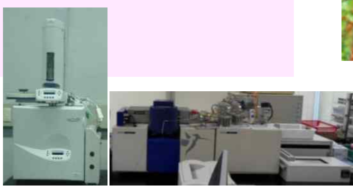
- **마늘** : 동위원소, 다중원소 이용 (*Food Control*, in revision)
- **양파** : 동위원소이용 (*Food Control*, 2019)
- **맥주** : 동위원소, 다중원소 이용 (*Food Control*, 2016)
- **한약재** : 다중원소, NMR 이용 (*Food Chemistry*, 2014)
- **고추, 쌀** : 스트론튬 동위원소 이용 (*J. Agric. Food Chem. 2014*)
- **배추** : 다중원소, 스트론튬 동위원소 이용 (*Food Chemistry, Food Control*, 2013)
- **김치** : 다중원소, 스트론튬 동위원소 이용 (*Biosci. Biotechnol. Biochem.* 2012)
- **휘발유** : 탄소, 수소 동위원소 이용 (*Rapid Commun. Mass Spectrom.* 2012)
- **인삼** : 다중원소, 스트론튬 동위원소, NMR 이용 (*J. Agric. Food Chem.* 2011)
- **쇠고기** : 탄소, 질소, 산소 동위원소 이용 (*Rapid Commun. Mass Spectrom.* 2010; *Food Sci. Biotechnol.*, 2012)
- **생수** : 산소, 수소 동위원소, 다중원소 이용 (*Anal. Chim. Acta* 2009)
- **과일, 채소 주스** : 산소, 수소 동위원소 이용 (*Rapid Commun. Mass Spectrom.* 2008)

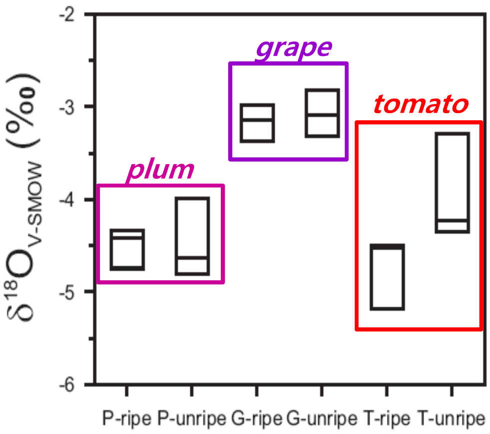
◆ **연구과제 수행** (농림축산식품부, 2016년~2019년):

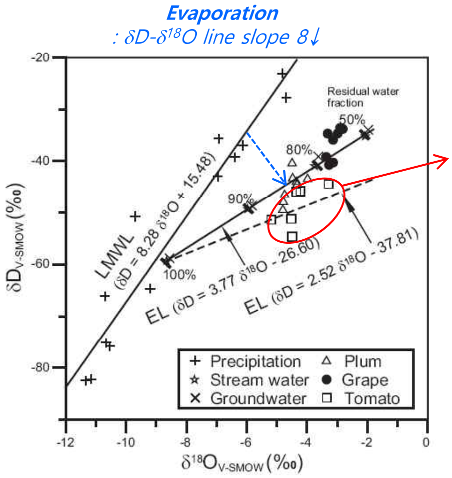
다중동위원소를 이용한 농산물시료(쌀, 마늘, 양파)의 원산지 추적 및 동위원소 광역지도 개발

식품의 진위 판별

- *채소와 과일 주스의 진위 판별법*
- *산소, 수소 동위원소 이용*



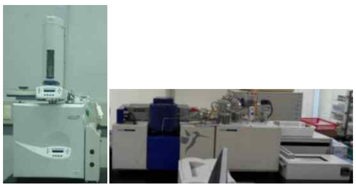


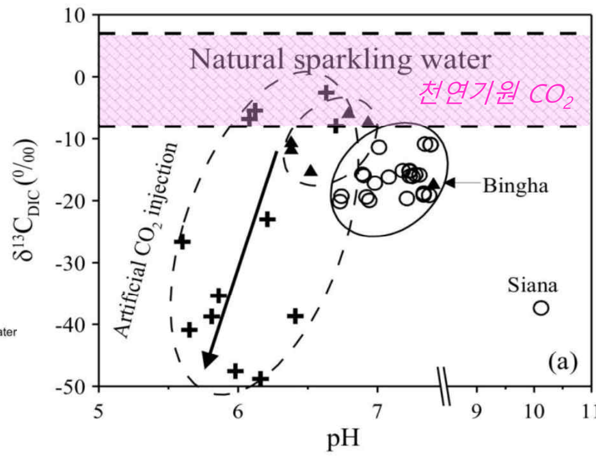


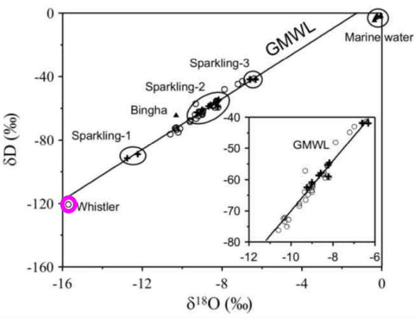
(Bong et al., 2008, RCM)

식품의 진위 판별

- *생수의 원산지 판별, 탄산수 진위 판별*
- *탄소, 산소, 수소 동위원소 이용*



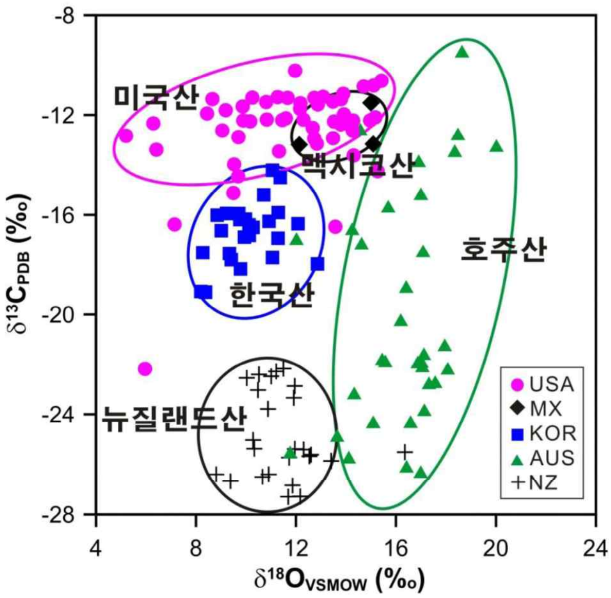




(Bong et al., 2009, ACA)

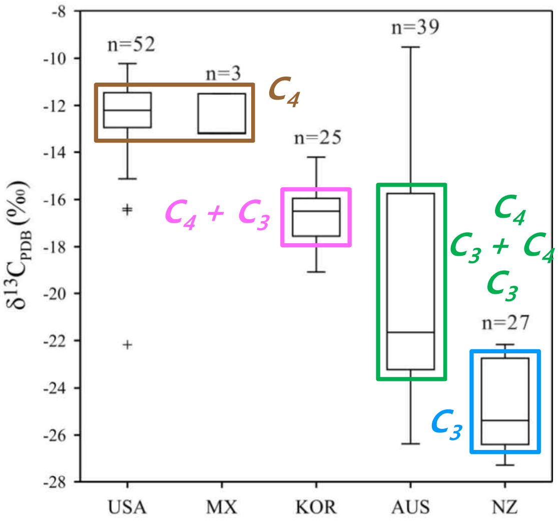
식품의 원산지 판별

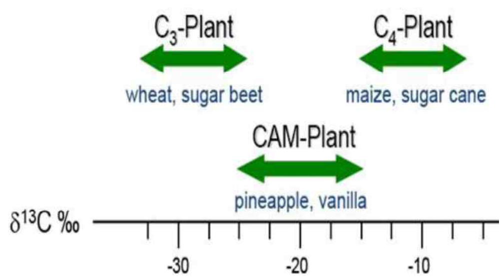
- 쇠고기의 원산지 판별법
- 탄소, 질소, 산소 동위원소 이용



(Bong et al., 2008, RCM; Bong et al., 2012, FSB)

탄소 안정 동위원소 분석 결과





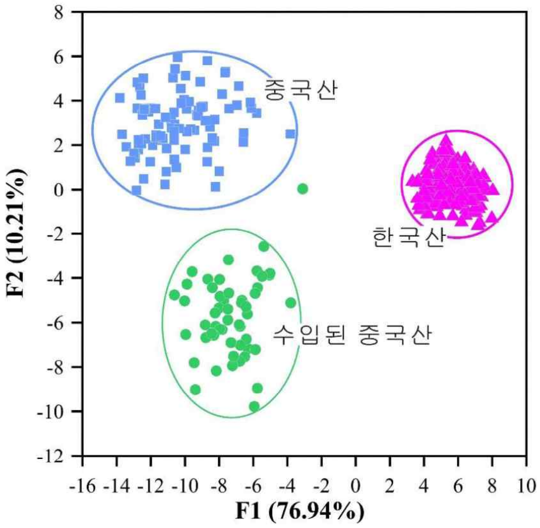
▶ Carbon isotope composition : feed type used for the cattle

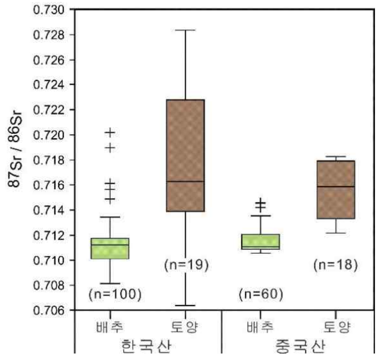
⇒ *C_4 plants (e.g. maize) : higher $\delta^{13}C$ values*

⇒ *C_3 plants (e.g. grass) : lower $\delta^{13}C$ values*

식품의 원산지 판별

- *배추의 원산지 판별법*
- *스트론튬 동위원소, 다중원소 이용*

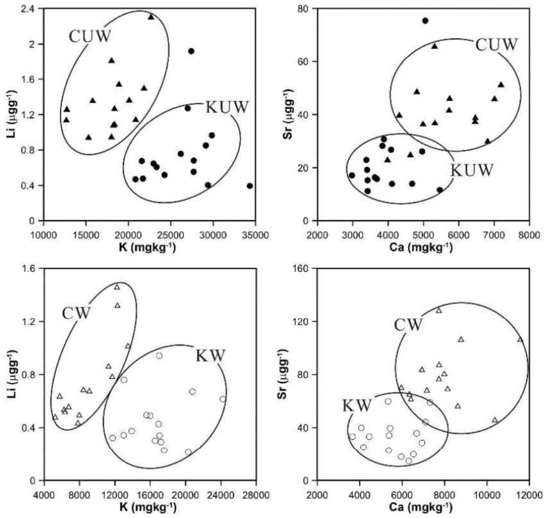


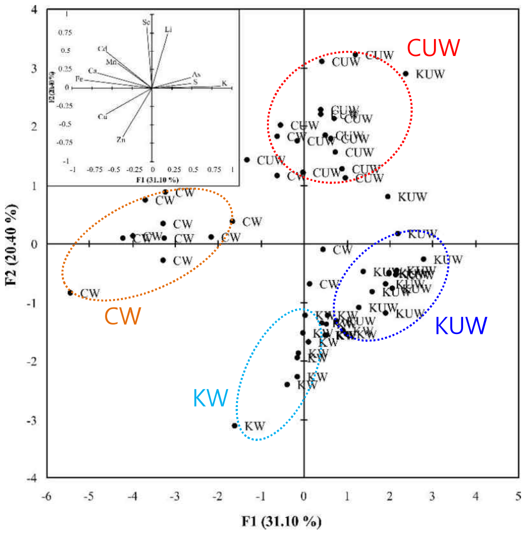


(Bong et al., 2012, Food Chem.; Bong et al., 2013, Food Control)

식품의 원산지 판별

- *김치의 원산지 판별법*
- *스트론튬 동위원소, 다중원소 이용*

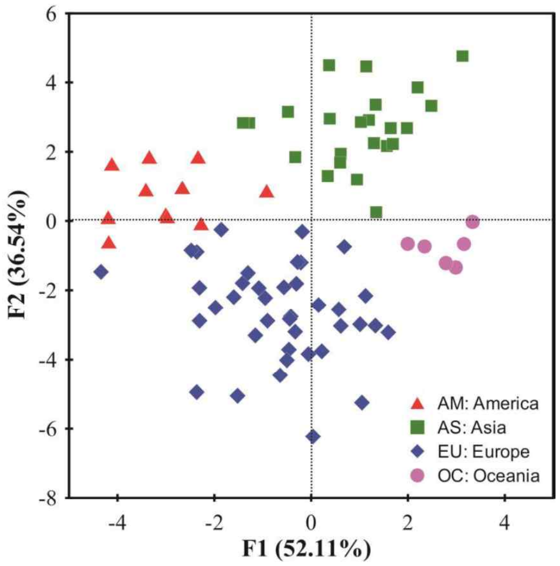




(Bong et al., 2012, Biosci. Biotechnol. Biochem.)

식품의 원산지 판별

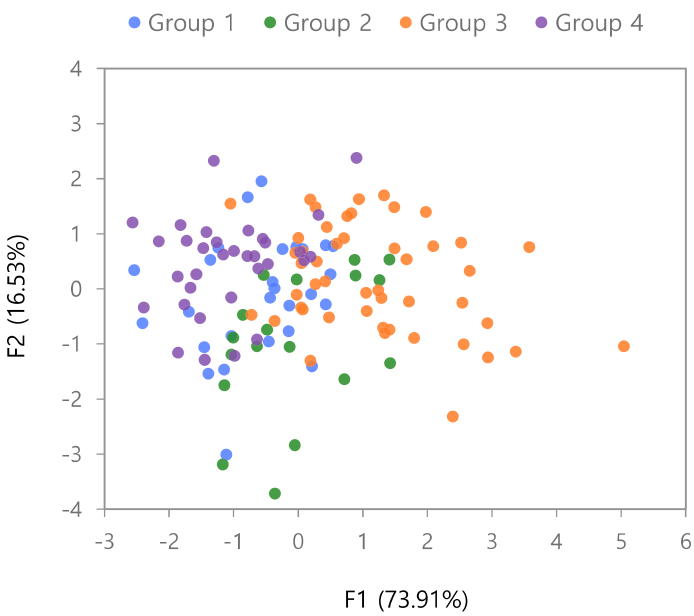
- 맥주의 대륙별 원산지 판별법
- 탄소, 산소, 스트론튬 동위원소 이용

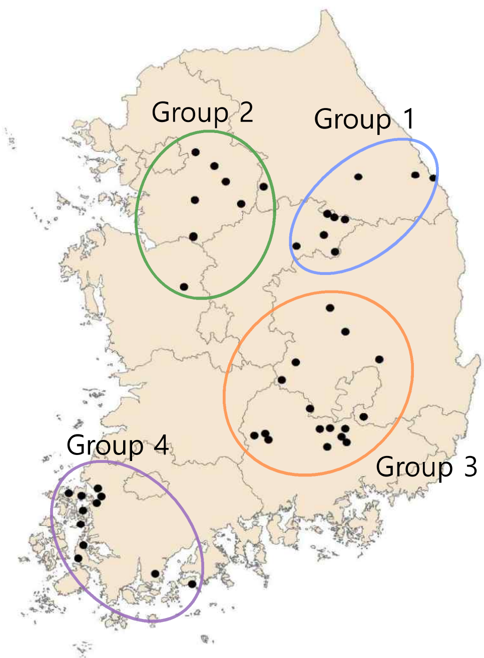


(Bong et al., 2016, Food Control)

양파의 원산지 판별

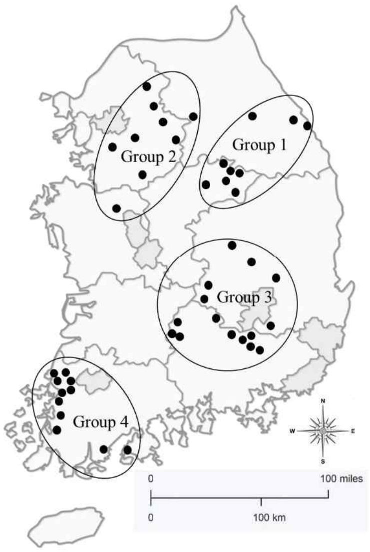
- *다중 동위원소 이용: 탄소, 질소, 황, 산소, 수소 안정 동위원소 분석*
  - 분석시료 수: 132개(+100개)

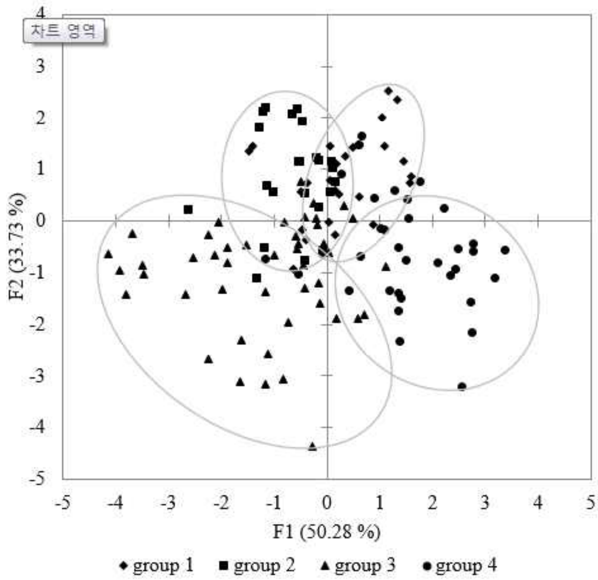




양파의 원산지 판별

- *다중 동위원소 이용: 탄소, 질소, 황, 산소, 수소 안정 동위원소, 각 원소 함량(%) 분석*
  - 분석시료 수: 130개(2017년 시료)

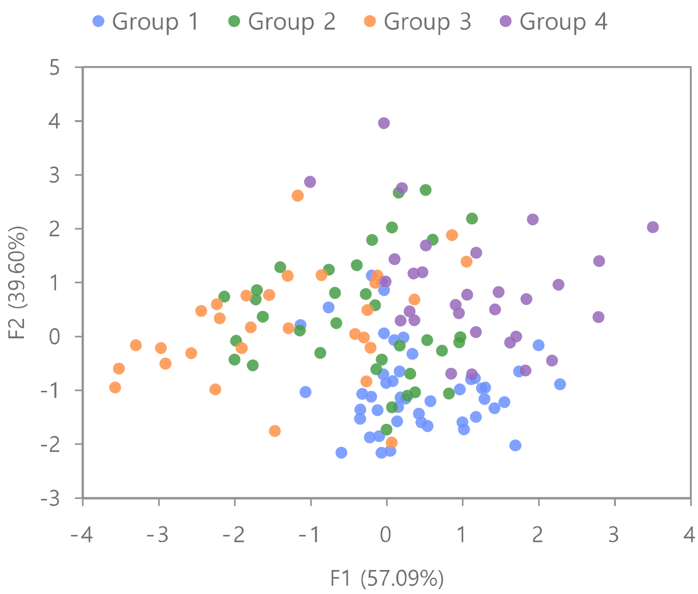


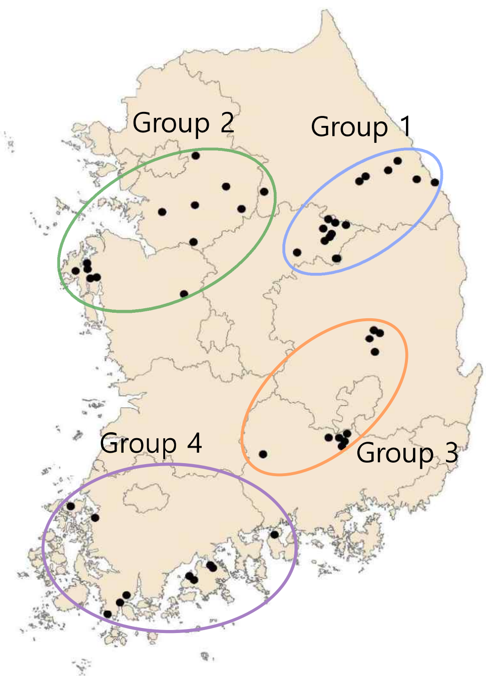


(Food Control, 2019), JCR 상위 10%

마늘의 원산지 판별

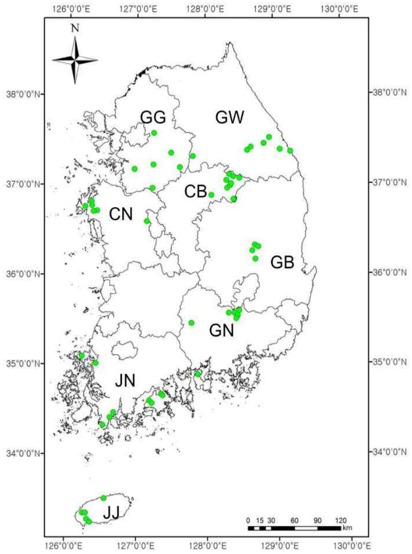
- *다중 동위원소 이용: 탄소, 질소, 황, 산소, 수소 안정 동위원소 분석*
  - 분석시료 수: 142개(+100)

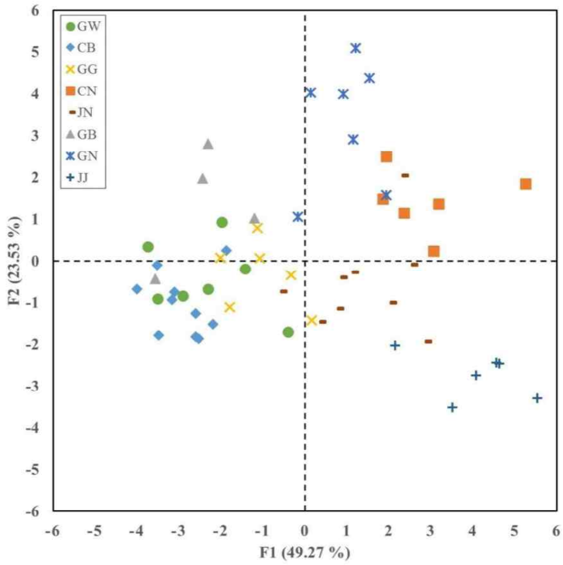




마늘의 원산지 판별

- *다중 동위원소 이용: 탄소, 질소, 황, 산소, 안정 동위원소, 다중원소 분석*
  - 분석시료 수: 130개(2017년 시료)





(Food Control, 2020), JCR 상위 10%

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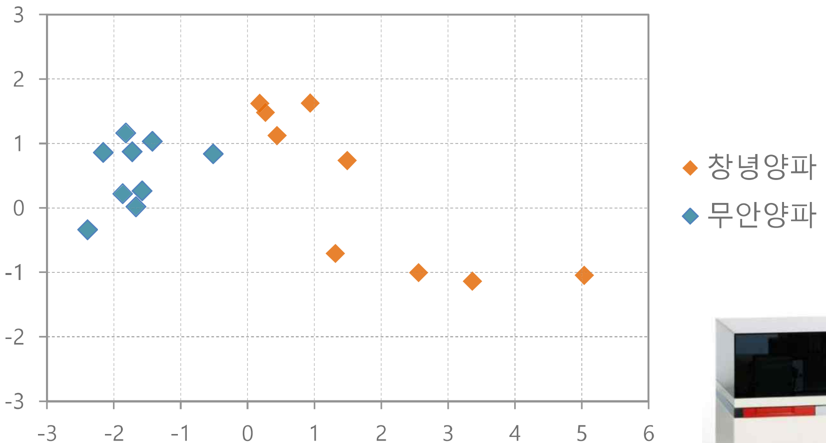
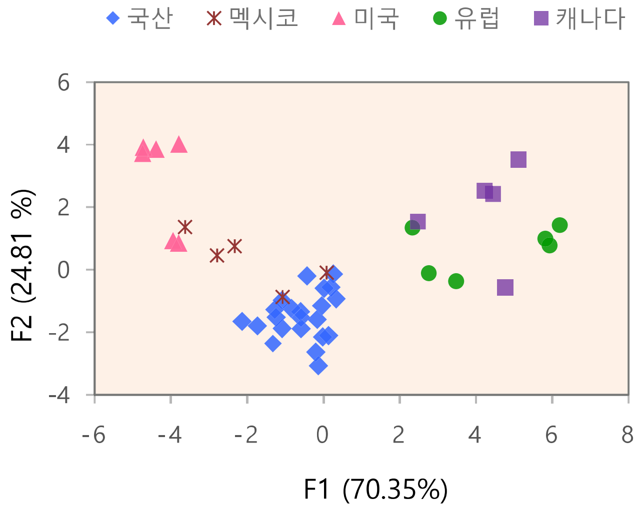
양파의 지리적 원산지 판별

- *지리적 표시제(GIS: Geographical Indication System)*
  : 창녕양파, 무안양파



돼지고기의 원산지 판별

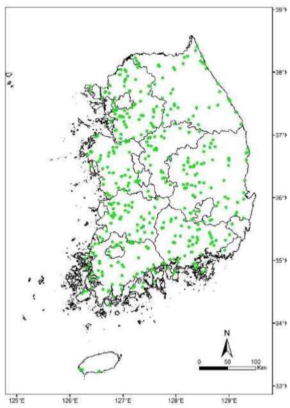
다중 동위원소 이용: 탄소, 질소, 황 안정 동위원소 분석
-분석시료 수: 44개(+200개)

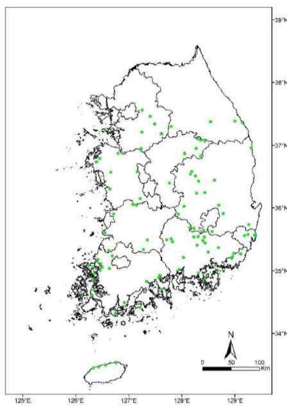


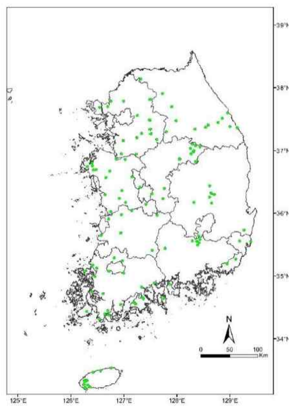
	국산	멕시코	미국	유럽	캐나다	Total	% correct
국산	22	0	0	0	0	22	100.00%
멕시코	2	2	1	0	0	5	40.00%
미국	0	2	4	0	0	6	66.67%
유럽	0	0	0	5	1	6	83.33%
캐나다	0	0	0	2	3	5	60.00%
Total	24	4	5	7	4	44	81.82%

원산지 시료 채취 및 분석

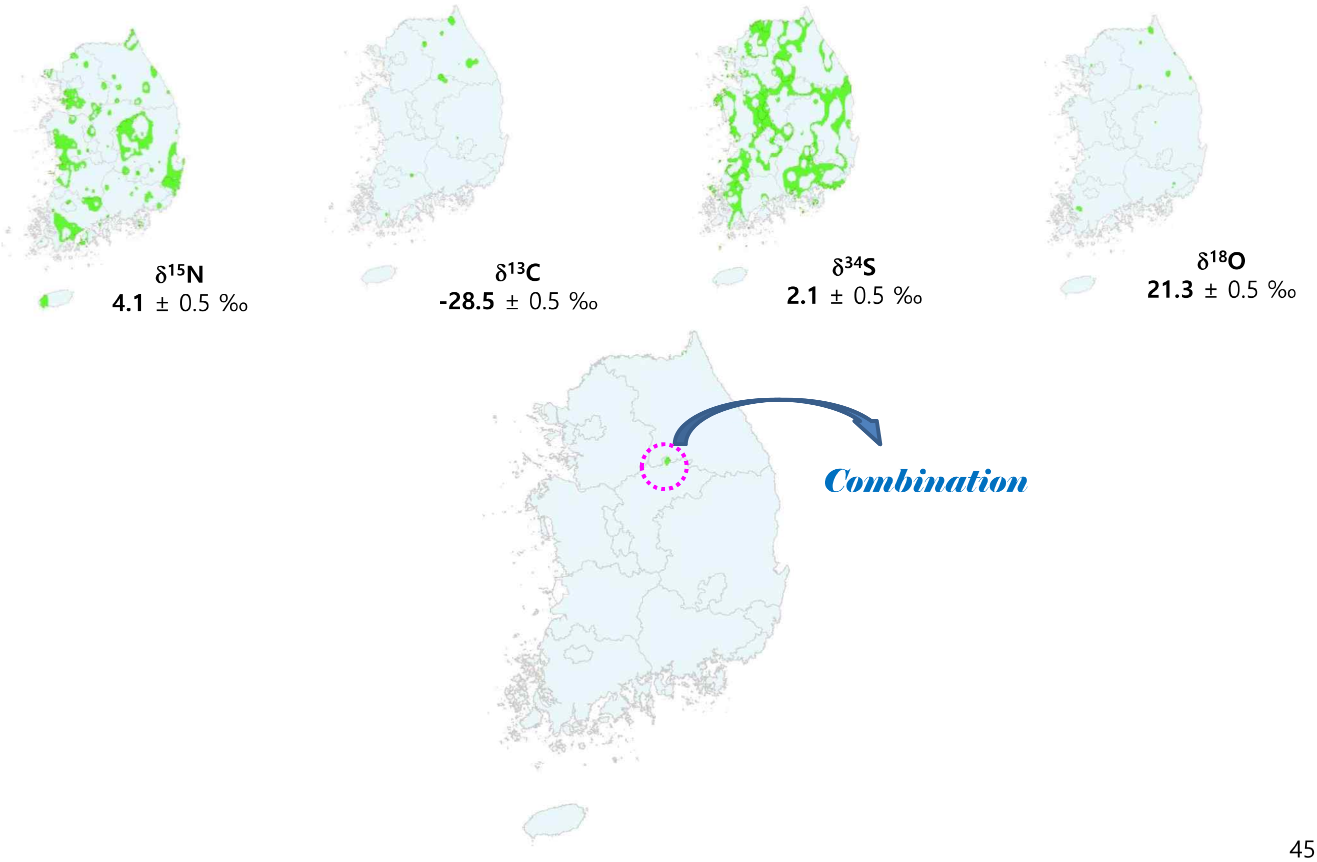
시료종류	계획	채취완료	분석완료
쌀	250	514	514
양파	250	256	256
마늘	250	288	288
물시료	500	466	466
토양	500	788	123
돼지고기	-	38	38


쌀시료

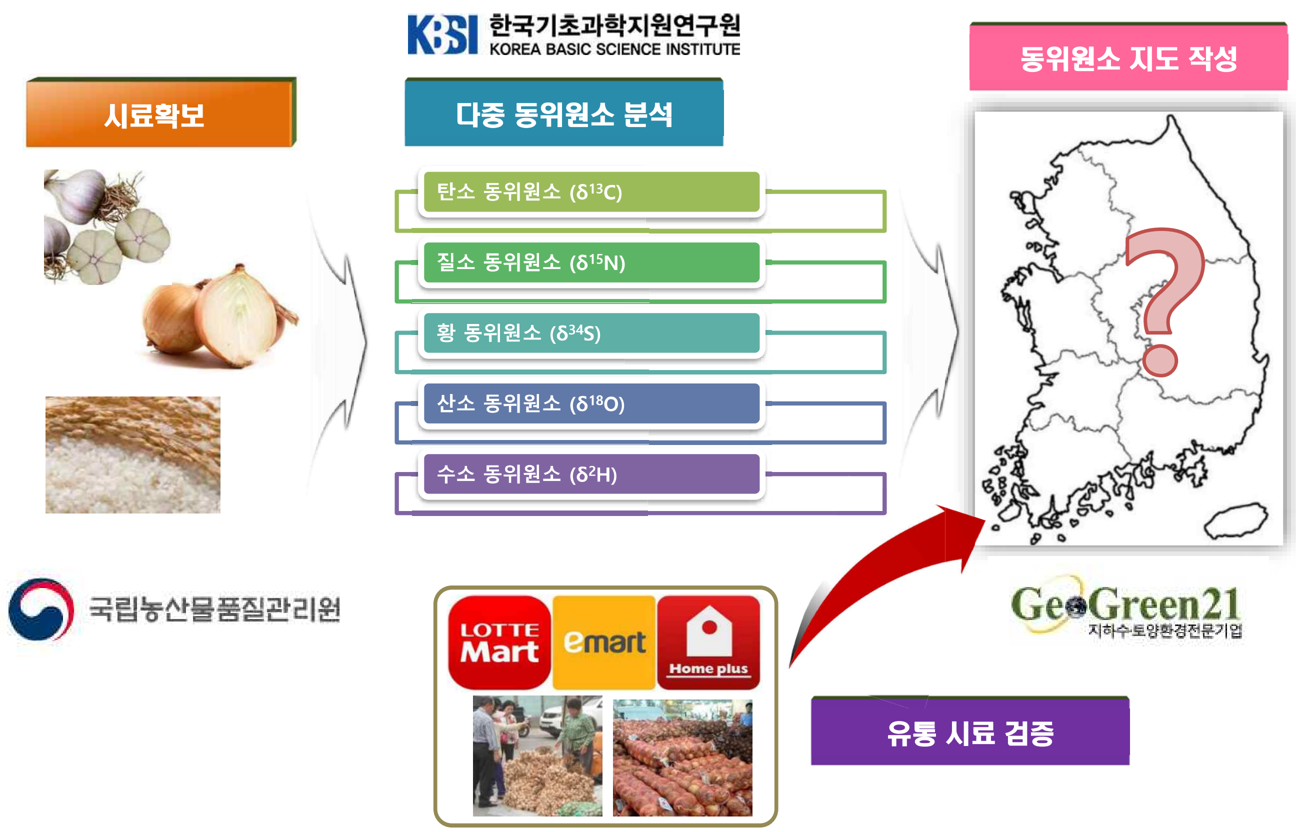

양파시료


마늘시료

Raster Calculator



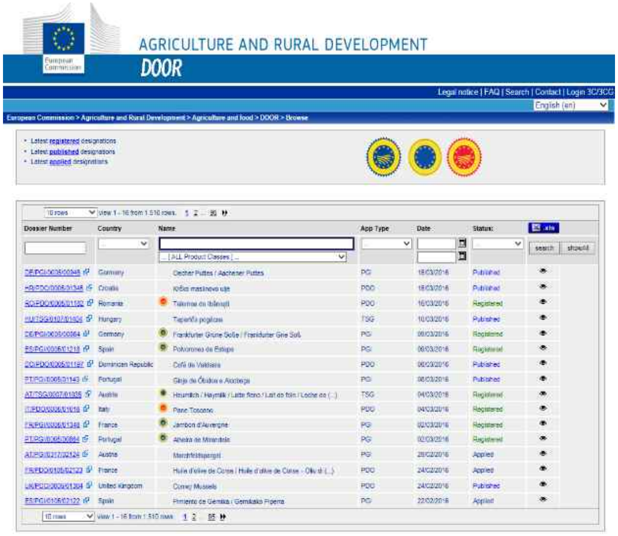
농산물 원산지 추적을 위한 동위원소 광역지도 개발



농산물 원산지 추적을 위한 동위원소 광역지도 개발

한국형 원산지 인증 제도 마련

- EU DOOR (Database of Origin and Registration)와 같은 인증 프로그램을 우리 농축산물에 맞도록 적용하여 **한국형 원산지 인증제도를 마련**



EU의 원산지 보호표시제, PDO

EU의 지리적 표시제, PGI

감사합니다

과학으로 지키는 국민행복,

with KBSI!

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3

납 동위원소 분석 및 산지 추정 연구 활용

정연중 (한국기초과학지원연구원)

충남연구원 세미나

납 동위원소 분석 및 산지 추정 연구 활용

2020. 02. 24.

한국기초과학지원연구원
정 연 중

KBSI 한국기초과학지원연구원 KOREA BASIC SCIENCE INSTITUTE

동위원소

KBSI 한국기초과학지원연구원 KOREA BASIC SCIENCE INSTITUTE

Isotope :

- ✓ 동위원소(isotope)는 원자번호는 같지만 원자량이 다른 원소를 말한다.
- ✓ 동중원소(isobar)는 원자번호는 다르지만 질량수가 같은 원자핵을 말한다.
- ✓ 동중성자핵(isotone)은 질량수는 다른지만 중성자의 개수는 같은 원자핵을 이야기한다.
- ✓ 한 원소의 동위원소 상대적 존재비 변화에 따라 화학적 반응 및 환경변화에 이용 (예: 해수와 지하수에서의 동위원소 존재비)

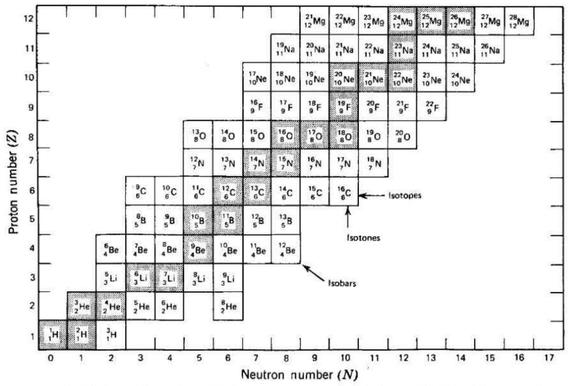
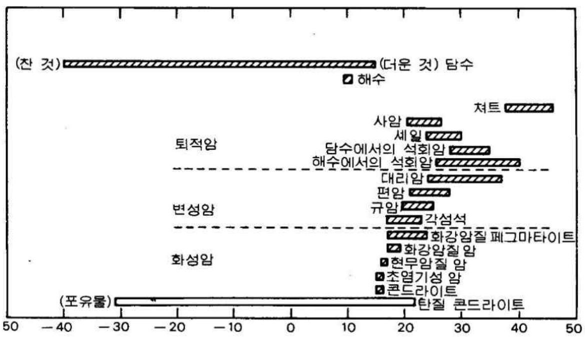


FIGURE 1.1 Partial chart of the nuclides. Each square represents a particular nuclide defined in terms of number of protons (Z) and neutrons (N) that make up its nucleus. The shaded squares represent stable atoms, whereas the white squares are the unstable or radioactive nuclides. Isotopes are atoms having the same Z but different values of N. Isotones have the same N but different values of Z. Isobars have the same A but different values of Z and N. Isotopes are atoms of the same element and therefore have identical chemical properties.



동위원소

동위원소

- 안정동위원소 (stable isotope)
  - 자연상태에서의 동일원소 안정동위원소의 존재비는 지구상에 일정하다.(방사성동위원소를 제외한 원소들)
- 방사기원 동위원소 (radiogenic isotope)
  - 특유의 에너지를 가진 방사선을 방출하고 안정된 동위원소로 붕괴(자연계에 약 14종의원소가 존재)

방사기원 동위원소

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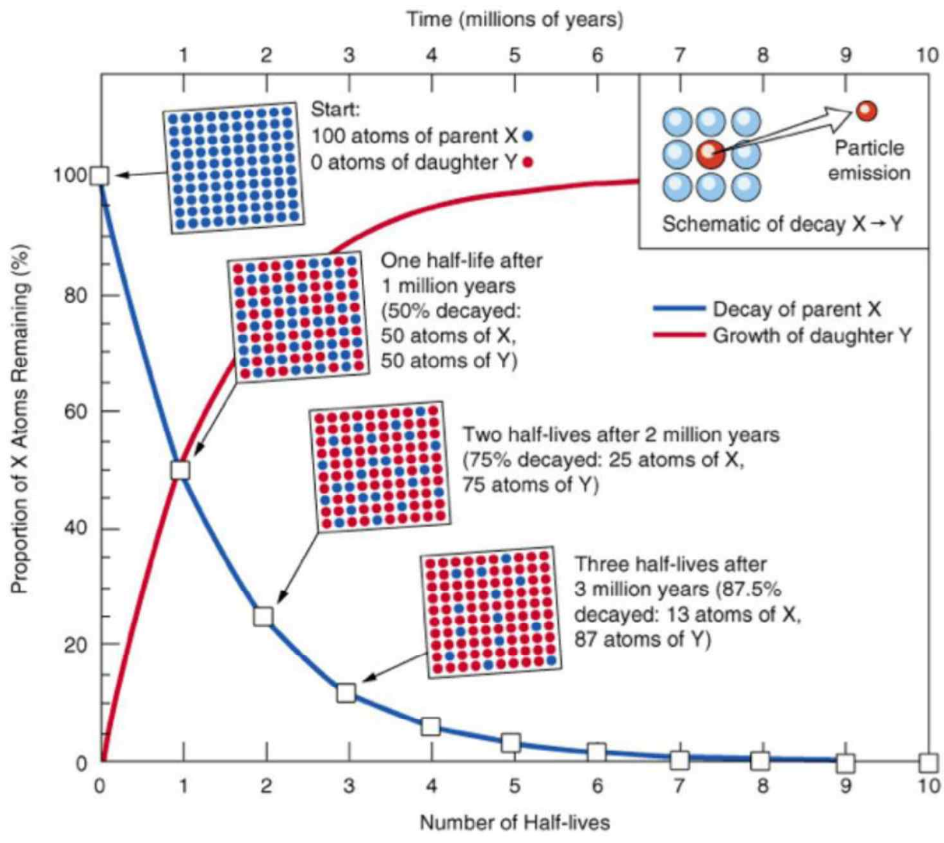
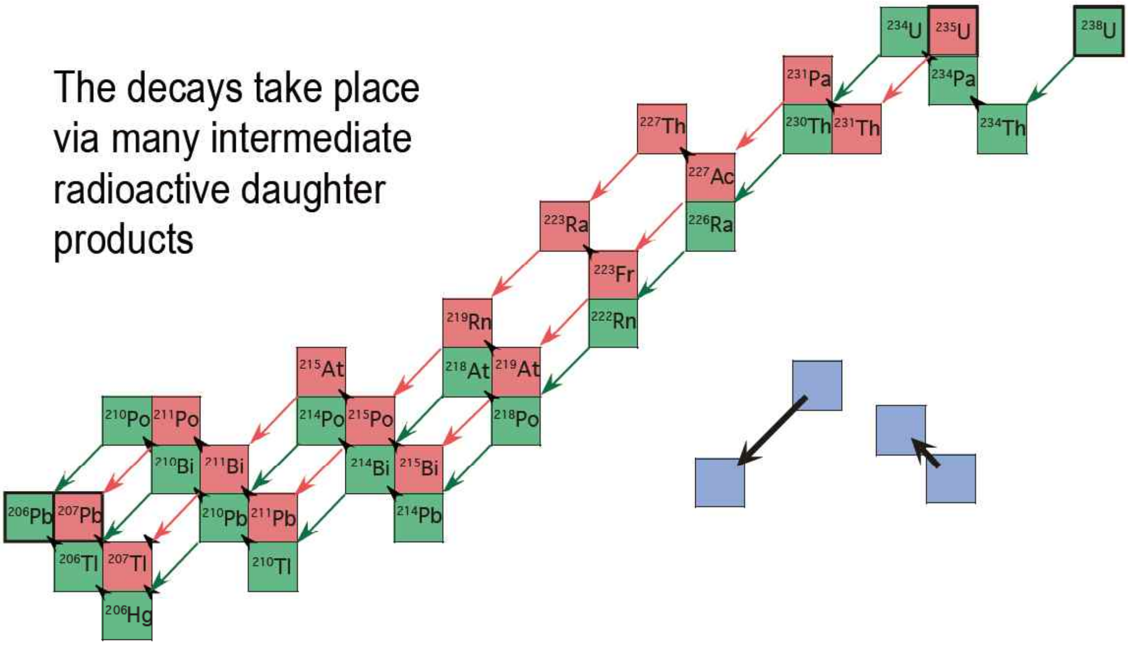


방사기원 동위원소

The U-Pb technique

The decays take place via many intermediate radioactive daughter products



연구장비 운영부 연대측정 장비

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SHRIMP (고분해능 이차이온질량분석기)

U, Pb, Rb, Sr, Sm, Nd, Ar, Hf, Lu
등의 방사기원 동위원소 분석

TIMS
(열이온화질량분석기)

SVMS
(비활성기체질량분석기)

LA-MC-ICP-MS
(레이저삭박 다검출기
유도결합플라즈마 질량분석기)

납 동위원소

^{204}Pb	^{206}Pb	^{207}Pb	^{208}Pb
203.97	205.97	206.98	207.98
1.40%	24.1%	22.1%	52.4%
stable	Radiogenic	Radiogenic	Radiogenci

Isotope ratio

$^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$
$^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$

납 동위원소 분석장비(TIMS)

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Thermal ionization mass spectrometer(TIMS)

Isoprobe-T TIMS
(IsotopX)

Phoneix TIMS
(IsotopX)

납 동위원소 분석장비(MC-ICPMS)

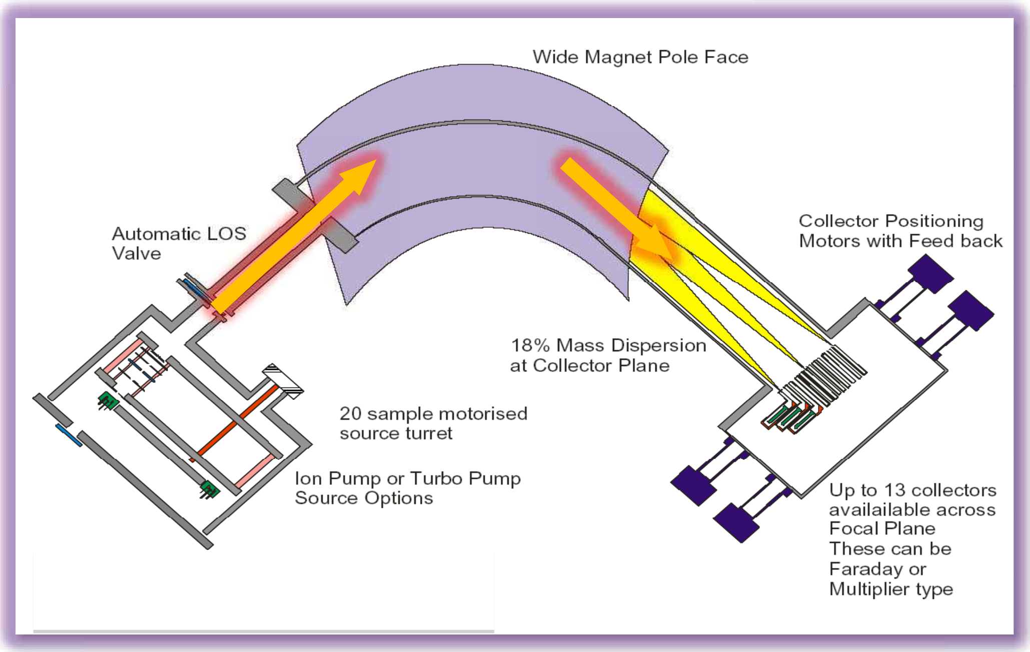
Multi Collector Inductively Coupled Plasma Mass Spectrometer(MC-ICPMS)

Nepture MC-ICPMS (Thermo Scientific)

Nu Plasma III (Nu instruemts)

납 동위원소 분석장비(TIMS)

Fundamental principles of TIMS



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Clean room(< 200 class)

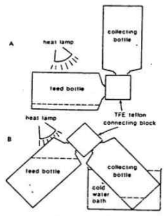

Figure Simple sub-boiling Teflon still comprising two FEP Teflon bottles (one feed, the other collecting) joined by a TFE Teflon connecting block, as designed by Mattinson (1972).

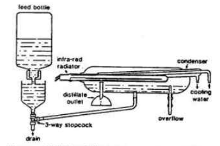

Figure Sub-boiling still made of quartz as designed by Kuehner et al. (1972).

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Column chemistry

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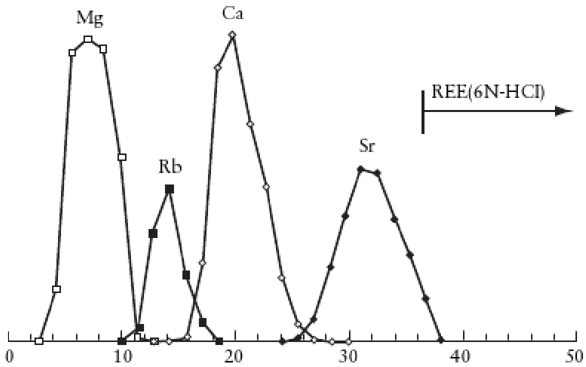
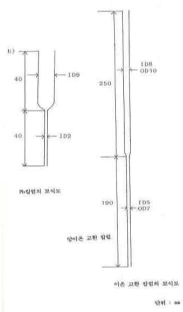
Elution pattern of column chemistry





시료에서 동위원소 분석을 위한 원소들의 분리를 위한 양이온 컬럼화학 Rb, Sr, REE & total Pb 등으로 분리한다

납 동위원소 분석 전처리 실험

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Filament loading for TIMS analysis

유물의 산지 추정을 위한 납 동위원소 활용

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유물의 산지 추정을 위한 납 동위원소 활용

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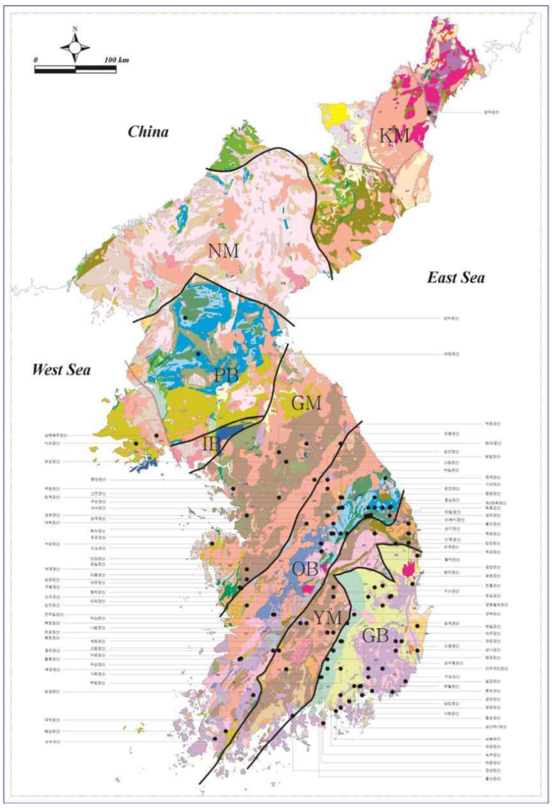
한반도 납동위원소

지구조 분포도 작성

➢ 한국의 지구조를 나타낸 지질도

➢ 2010~2013년 까지 조사된

방연석광산 총 106개 광산표시



한반도 금속광산의 납 동위원소 지도

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Geosciences Journal

Lead isotope mapping of galena from base metal deposits in the southern Korean Peninsula

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ABSTRACT: The purpose of this study is to investigate the differences in sources of discrete four zones that are represented by the lead isotope map of metal mines using galena samples. The lead isotope map has been constructed based on 119 galena samples from 38 metal mines in the southern Korean Peninsula, together with previously published data, using spatial and zoning distribution analysis. The spatial pattern of $^{206}Pb/^{204}Pb$ ratio shows relatively dense distribution with highest value at the northeastern region, while $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios are the lowest at the southeastern region. These results indicate possible subdivision of the lead isotope maps based on geotectonic subdivisions and geographical locations of the Korean Peninsula. This subdivision has been checked by linear discriminant analysis (LDA). The range of lead isotopic composition for zone 1 has fairly homogeneous values ($^{206}Pb/^{204}Pb$ = 18.156–18.591, $^{207}Pb/^{204}Pb$ = 15.482–15.644, and $^{208}Pb/^{204}Pb$ = 37.870–38.768), and are geographically similar to the Gyeongsang Basin. Lead isotopic compositions of zone 2 show the highest ratios ($^{206}Pb/^{204}Pb$ = 18.625–20.483, $^{207}Pb/^{204}Pb$ = 15.708–16.068, $^{208}Pb/^{204}Pb$ = 37.734–40.463) in the southern Korean Peninsula, that are geographically corresponding to the Taebaeksan Basin and the northeastern Yeongnam Massif. Relatively lower values ($^{206}Pb/^{204}Pb$ = 17.149–17.817, $^{207}Pb/^{204}Pb$ = 15.497–15.731, $^{208}Pb/^{204}Pb$ = 37.847–39.773) along the western Gyeonggi Massif are grouped as zone 4, while the rest of the areas, including the Okcheon metamorphic belt, most of the Gyeonggi Massif, and the Yeongnam Massif, might represent zone 3. The results clearly indicate the possible differences in the source reservoirs that are similar to the geotectonic provinces of the Korean Peninsula.

Key words: lead isotope map, galena, metal mines, southern Korean Peninsula

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1. INTRODUCTION

Lead isotopic composition records the age according to U/Pb and Th/Pb as well as geochemical properties of origin materials (Cumming and Ricahrds, 1975; Doe and Zartman, 1979; Zartman and Doe, 1981; Zartman and Haines, 1988; Zhu, 1995), and can be applied as a useful tool for the provenance investigations, to identify the source of pollution about environment samples, to reveal the correlation of the origin between bronze relics and raw material and to explore the ore deposits (Gulson, 1986; Mukai et al., 1994; Gale and Stos-Gale, 2000; Nie et al., 2002; Gökce and Bozkaya, 2005).

The sulfide mineral including galena, the focus of this study, is generally easy to analyze the lead isotope ratio because of their sufficient amount of the lead element, and has almost zero U/Pb. Because galena is the main ore of lead among the sulfide ore deposits, lead isotopic composition of it indicates the characteristics in the reservoir within earth's crust and mantle (O'Nions et al., 1979). Thus, it generally represents the geotectonic provinces than the internal earth's structures (Zhu, 1995).

This study constructs the lead isotope map using galena samples from metal mines in the southern Korean Peninsula, indicating characteristic distributions in lead isotope ratios in the southern Korean Peninsula. The results will show differences in the basement sources of the four subdivided zones based on the lead isotope map of metal mines that are similar to the geotectonic provinces of the Korean Peninsula.

2. GEOGLOGICAL BACKGROUND AND SAMPLE COLLECTION

The southern Korean Peninsula is comprised of four northeast-trending geotectonic provinces (Chough et al., 2000; Jeong et al.,

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한반도 납 동위원소 광역분포도

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- GM : 경기육괴 13점
- OB : 옥천대(태백산분지포함) 34점
- YM : 영남육괴 15점
- GB : 경상분지 39점

총 101개 광산 346점 시료 채취

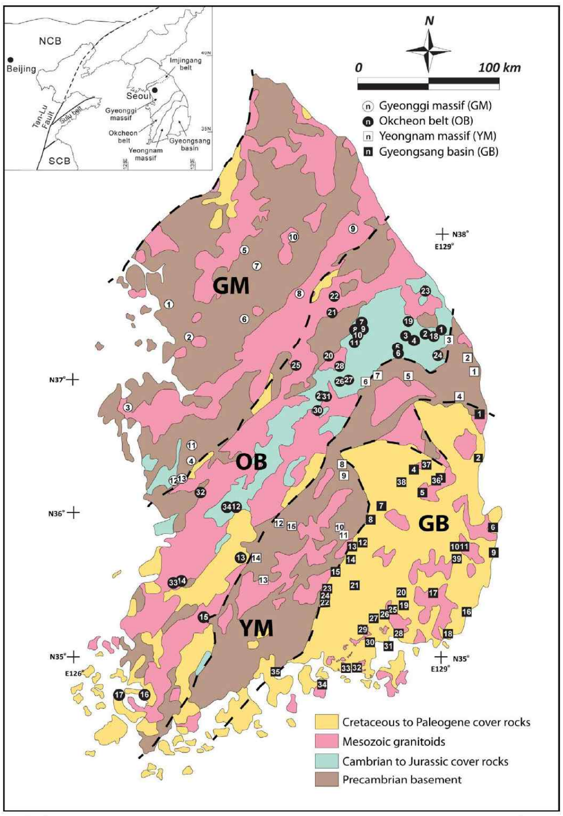

Fig. 1. Simplified geologic map (modified after Chough et al., 2000; Jeong et al., 2012) showing locations of the examined metal mines in the southern Korean Peninsula. Dashed lines represent boundaries between the geotectonic provinces.

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Table 1. Description of examined metal mines in the southern Korean peninsula

Deposit No.	Name	Location[(a)]	Ore type	Host rock	Ore mineral[(b)]	Associated mineral[(b)]	Age (Ma)	References
Gyeongsang basin								
GB 3	Cheongsong	GB Cheongsong	hydrothermal	sandstone, shale	Cp, Gn, Sp	Py		
GB 36	Jiso	GB Cheongsong	hydrothermal	sandstone, shale	Cp, Gn, Sp	Py, Ma, Ar		
GB 37	Jeonheung	GB Uiseong	hydrothermal	sandstone, shale	Cp, Gn, Sp	Py, Ma		
GB 38	Ohto	GB Uiseong	hydrothermal	sandstone, shale	CP, Gn, Sp, Tro	Py, Mt, Hm, Ma	70.5	Lee et al. (1993)
GB 39	Changgang	GB Gyeongju	hydrothermal	andesite	Au, Ag	Gn, Sp, Cp, Py		
Yeongnam massif								
YM 2	Uljin	GB Uljin	skarn	limestone	Gn, Sp	Ar, Cp, Asp, Mt, Po, Py	49.3 ± 2.0	Yun and Silberman (1979)
YM 4	Janggun	GB Bonghwa	hydrothermal	limestone	Gn, Sp	Au, Ar, Cp, Asp, Po, Py	78	Park et al. (1988a)
YM 13	Bunam	JB Jangsu	hydrothermal	biotite banded gneiss	Au, Ag	Gn, Py		
YM 14	Baekwon	JB Jinan	hydrothermal	granodiorite	Au, Ag	Gn, Sp, Cp, Asp, Tro, Py		
YM 15	Narim	CB Yeongdong	hydrothermal	biotite granite gneiss, porphyry granite	Au, Ag, Mt, He	Gn, Sp, Cp, Py, Asp		
Okcheon belt								
OB 5	Sinyemi	GW Jeongseon	hydrothermal	limestone	Gn, Sp	Cp, Mo, Po, Py	77.7 ± 2.0	Park et al. (1988a)
OB 18	Dunjun	GW Samcheok	hydrothermal	limestone, shale	Au, Ag	Gn, Cp, Tro	75.1 + 1.7	Lee (1993)
OB 19	Goyang	GW Jeongseon	hydrothermal	limestone, shale, sandstone	Mt	Gn, Sp, Tro		
OB 20	Shinrim	GW Wonju	hydrothermal	biotite schist	Au, Ag	Gn, Cp, Sp		
OB 21	Sanjeon	GW Hoengseong	hydrothermal	biotite granite	Gn, Sp, Cp, Asp	Au, Ar, Py		
OB 22	Cheongil	GW Hoengseong	hydrothermal	biotite granite	Au, Ag	Gn, Sp, Cp		
OB 23	Okgea	GW gangneung	hydrothermal	limestone	Au, Ag, Cu	Gn, Sp, Py, Asp		
OB 24	Samjo	GW Taebaek	hydrothermal	limestone	Au, Ag	Gn, Sp, Py		
OB 25	Daehwa	CB Chungju	hydrothermal	gneiss, grainte	Wf, Sch	Cp, Py, Mo, Gn	88.2 + 1.8	So et al. (1983); Park et al. (1985)
OB 26	Gumsil	CB Jecheon	hydrothermal	limestone, calc-silicate rock, black schist	Gn, Sp	Cp, Py, Asp, Tro	76.18 + 1.77	So and Yun (1992)
OB 27	Boksu	CB Jecheon	hydrothermal	limestone	Au, Ag	Gn, Sp, Py		
OB 28	Sanggok	CB Danyang	hydrothermal	limestone	Gn, Sp, Tro	Au, Ar		
OB 29	Chueun	CB Goesan	hydrothermal	phyllite	Au, Ag	Gn, Sp, Py, Tro		
OB 30	Manjang	CB Goesan	hydrothermal	limestone, phyllite	Cp, Asp, Mt	Gn, Sp, Tro		
OB 31	Insung	CB Goesan	hydrothermal	phyllite	Au, Ag	Gn, Sp, Cp, Py, Tro		
OB 32	Imchun	CN Buyeo	hydrothermal	granite gneiss, biotite granite	Au, Ag	Gn, Py		
OB 33	Palbong	JB Jeongeup	hydrothermal	schistose granite	Au, Ag	Gn, Sp, Cp, Py		
OB 34	Jeonjuil	JB Wanju	hydrothermal	phyllite, slate	Au, Ag	Cp, Gn, Py		
Gyeonggi massif								
GM 4	Samgwang	GN Cheongyang	hydrothermal	granite gneiss	Au, Ag	Cp, Gn, Sp, Asp, Py	127.1 ± 2.8	So et al. (1988)
GM 5	Dukdun	GG Pocheon	hydrothermal	granite gneiss	Au, Ag	Gn, Tro, Py		
GM 6	Cheonggye	GG Gwangju	hydrothermal	biotite gneiss, granite	Cp, Gn, Sp	Au, Ar		
GM 7	Bosung	GG Gapyeong	hydrothermal	biotite banded gneiss, sericite schist	Gn, Sp, Cp, Asp	Au, Ar, Py		
GM 8	Jungang	GW Hongcheon	hydrothermal	honblende granite	Au, Ag	Gn, Sp, Cp, Py		
GM 9	Weondae	GW Inje	hydrothermal	biotite granite, granite gneiss	Gn, Sp	Au, Ar, Py		
GM 10	Obong	GB Hawcheon	hydrothermal	two-micas granite	Au, Ag	Gn, Cp, Sp		
GM 11	Dukgok	CN Gongju	hydrothermal	granite gneiss	Au, Ag	Gn, Py, Mg		
GM 12	Gubong	GN Cheongyang	hydrothermal	biotite schist, granite gneiss	Au, Ag	Gn, Sp, Cp, Py		
GM 13	Daebong	GN Cheongyang	hydrothermal	mica schist, granite gneiss	Au, Ag	Gn, Sp, Cp, Asp, Py		

[(a)]Abbreviations: GB = Gyeongsangbuk-do, JB = Jeollabuk-do, CB = Chungcheongbuk-do, GW = Gangwon-do, CN = Chungcheonnam-do, GG = Gyeonggi-do, GN = Gyeongsangnam-do, CN = Chungcheongnam-do.
[(b)]Abbreviations: Gn = galena, Sp = sphalerite, Cp = chalcopyrite, Py = pyrite, Asp = arsenopyrite, Mt = magnetite, Sch = scheelite, Ma = malachite, Au = native gold, Ar = Argentite, Wf = wolframite, Tro = troilite, He = hematite, Mo = molybdenite.

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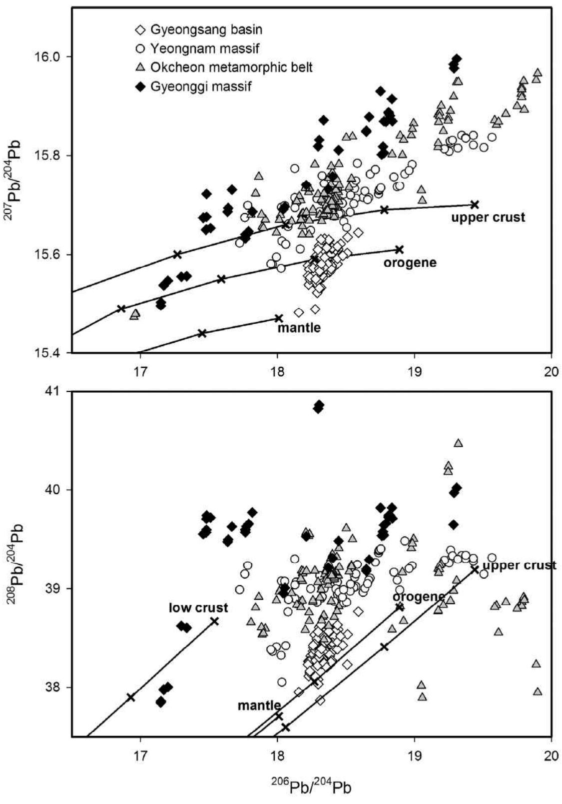

Fig. 2. $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ covariation diagrams for the galena samples from geotectonic provinces in southern Korean Peninsula. The growth curves of the upper crust, orogeny, mantle, and lower crust reservoirs are also given with 0.4 Ga increments after the plumbotectonic model of Zartman and Doe (1981).

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Table 3. The geotectonic characters, geographical location, number of mines and galena samples about discrete four zones

Zone	Geotectonic characters	Geographical location	No. mines	No. galena samples	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
Zone 1	Gyeongsang Basin	Gyeongsang-do	39	104	18.156~18.591	15.482~15.644	37.870~38.768	0.8146~0.8548	2.0687~2.1130
Zone 2	Taebaeksan Basin (internal Okcheon Belt), northeastern Yeongnam Massif	South Kangwon-do, North Gyeongsang-do	13	65	18.625~20.483	15.708~16.068	37.734~40.463	0.7839~0.8439	1.8464~2.1017
Zone 3	Okcheon Belt (exclude Taebaeksan Basin), Yeongnam Mssif (exclude northeastern regions), Gyeonggi Massif (exclude western regions)	Jolla-do, Chungcheong-do, Gyeonggi-do	43	156	16.953~19.566	15.473~15.996	36.703~41.001	0.8094~0.9126	2.0094~2.2399
Zone 4	Western Gyeonggi Massif	North Choengcheong-do, West Gyeonggi-do	6	21	17.149~17.817	15.497~15.731	37.847~39.773	0.8795~0.9049	2.2069~2.2782

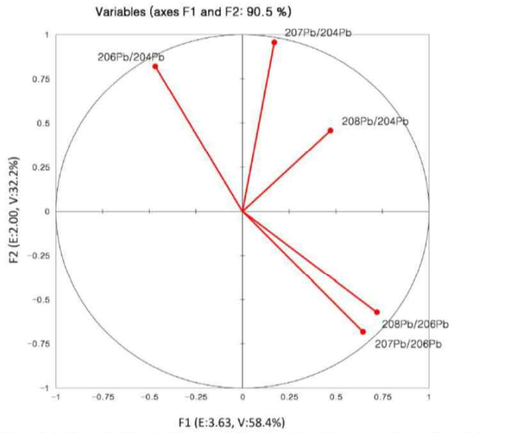

Fig. 4. Correlation circle plot showing the effects of each isotope ratios for the four subdivided zones using a diagram of F1 vs. F2 discriminant functions (E: eigenvalue, V: variance).

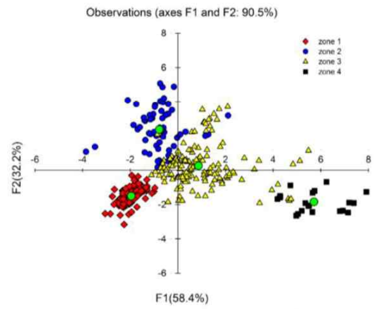

Fig. 5. Discriminant observation plot showing first two discriminant functions and separation of galena samples from discrete four zones.

Table 4. Classification confusion matrix after linear discriminant analysis based on lead isotopes values

From To	Zone 1	Zone 2	Zone 3	Zone 4	Total	% correct
Zone 1	104	0	0	0	104	100
Zone 2	0	61	4	0	65	93.9
Zone 3	6	5	145	0	156	93
Zone 4	0	0	0	21	21	100
Total	110	66	149	21	346	95.7

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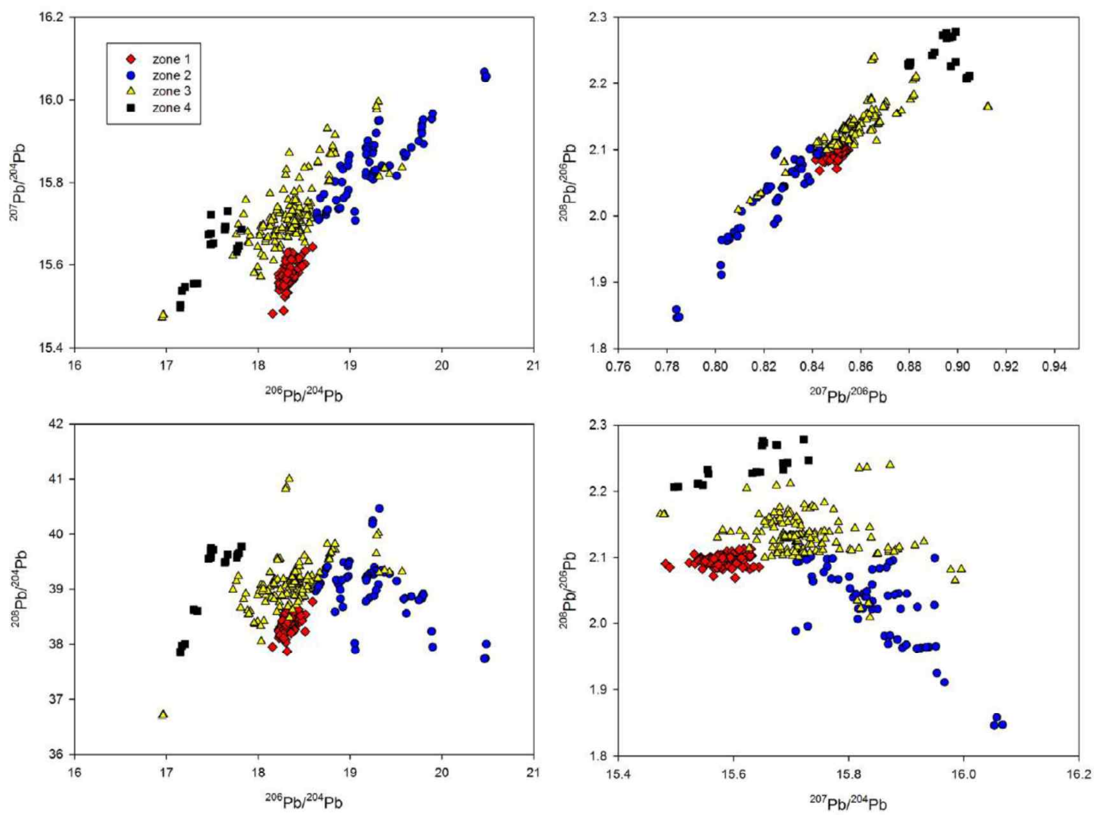

Fig. 6. Lead isotopic compositions of galena samples from discrete four zones in the southern Korean Peninsula.

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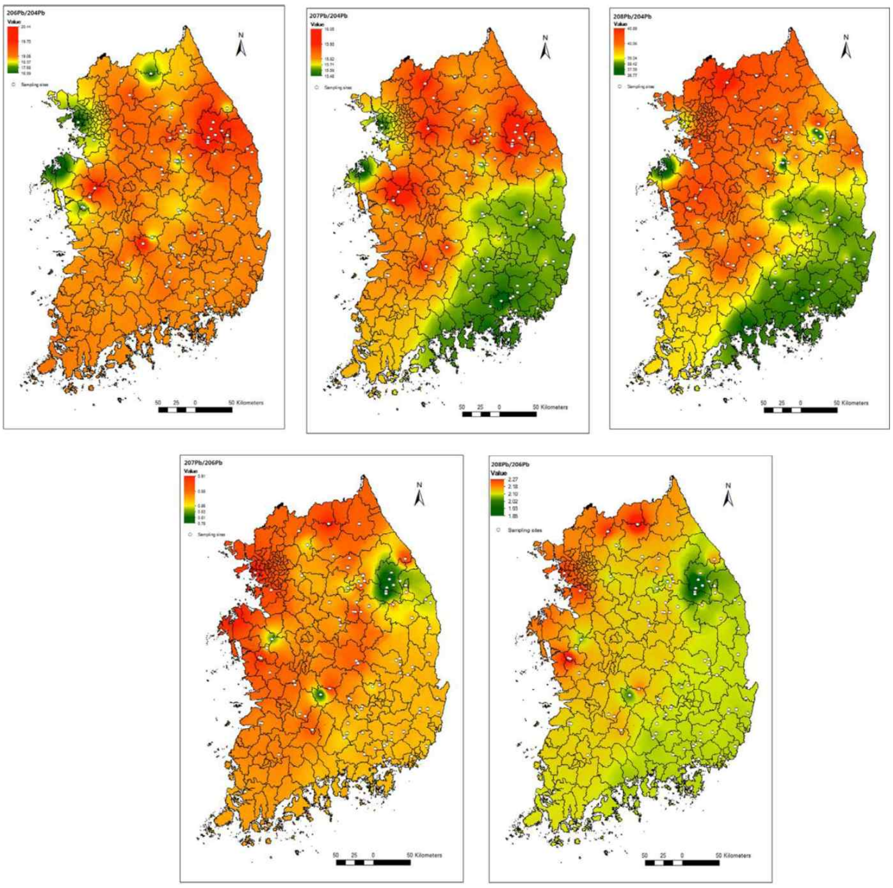

세형동검의 산지 추정

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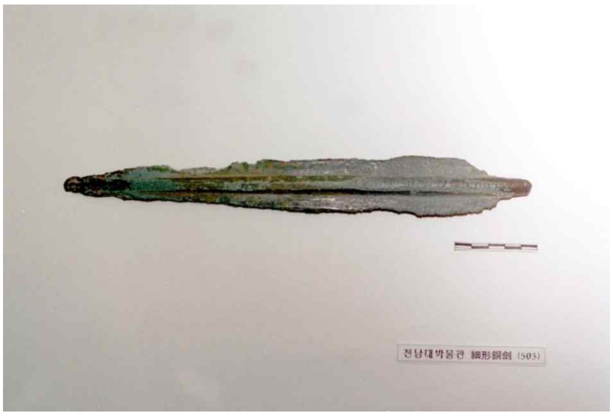
- 동검은 청동기시대 청동유물 중 대표적인 유물이며, 비파형동검과 세형동검으로 구분된다.
- 세형동검은 청동기 후기 대표적인 유물이며, 한반도에서 주로 출토되어 한국식 동검이라고도 불린다.
- 세형동검은 검신과 검병을 따로 만드는 조립식 동검 중 결입부가 형성되고 중앙에 굵은 등대가 있는 것으로 정의한다.
- 세형동검의 자연과학연구방법은 조성비연구, 미세구조관찰, 납동위원소비분석 등이 일반적인 연구방법이다.

Pb-14 세형동검(전북대 박물관)



Pb-27 세형동검(전남대 박물관)

세형동검의 산지 추정

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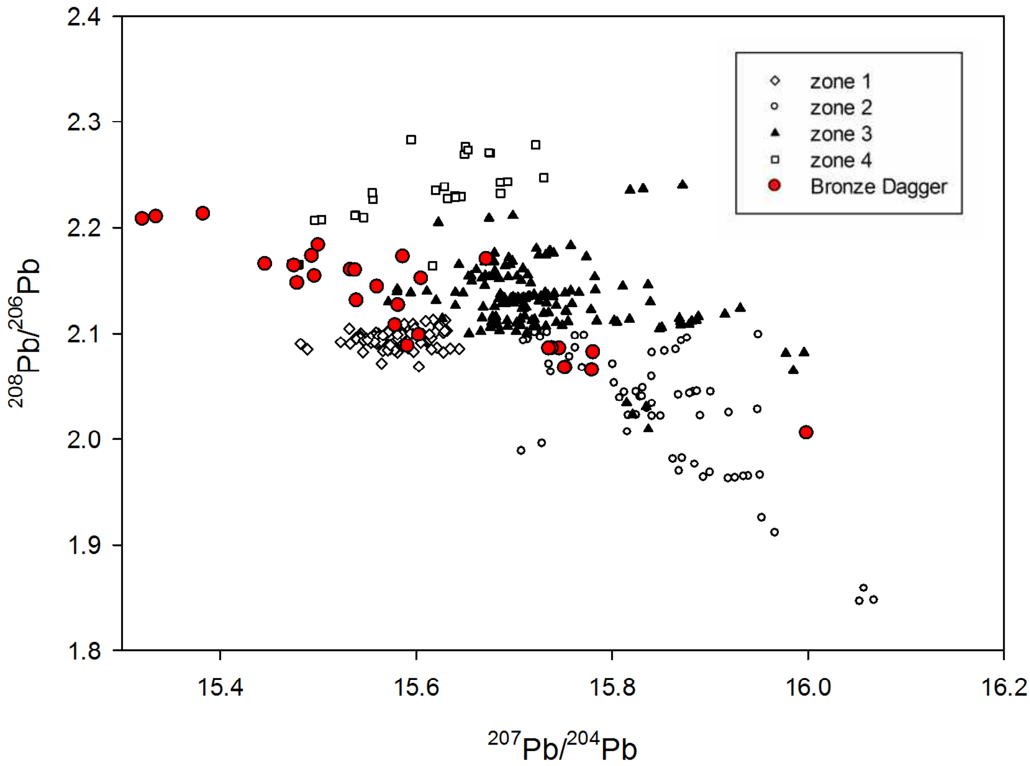

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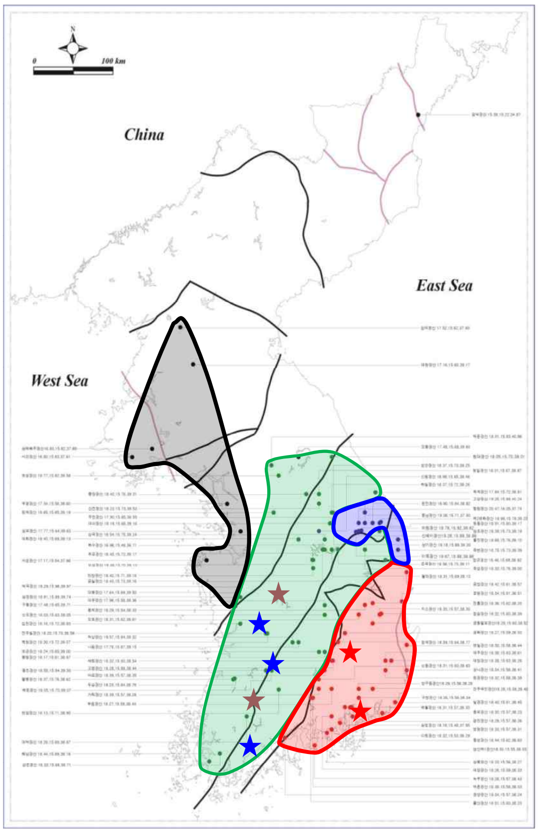
출토지: 전라도, 충청도
산지: zone 2

출토지: 전라도, 충청도
산지: 한반도 영역 외

출토지: 경상도, 산지: zone 1



오염토양의 원인자 추적 및 기여도 평가 활용

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미래를 읽는 환경경제뉴스

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대구환경청·산림청, 영풍석포제련

서창완 기자 | 승인 2018.11.30 19:28

중금속 침출수 낙동강 유입 진위 확인

석포제련소

[그린포스트코리아 서창완 기자] 환경·산림당국이 경
조사에 나선다.

대구지방환경청은 석포제련소 주변 침출수 조사를 우
최종 입찰은 12월 말쯤에 결정될 전망이다. 조사 기간

대구환경청 조사는 석포제련소 2공장 부근에서 중금
는 환경단체 주장이 사실인지 파악하기 위해 이뤄진

대구환경청 환경감시과 관계자는 "하천 주변 집수정
도 등이 있는데 우리 스스로 객관적 규명이 힘들어 용

조사는 석포제련소 2공장 주변 지하수 모니터링과
으로 진행될 예정이다.

전국 네트워크 | 미디어네트워크 | 제보하기

노컷뉴스

최신 정치 경제 사회 전국 연예 문화 세계 스포츠 포토

대구

안동댐 상류 중금속 오염 휴·폐

안동=대구CBS 권기수 기자 | 2017-10-21 10:06 뉴스듣기

홍의락 의원 "방지대책 신속히 추진해야"

중금속 오염으로 신음하는 안동댐 상류지역. (사진=자료사진)

안동댐 상류지역의 휴·폐광산 2곳 가운데 1곳이 중금속오
것으로 드러났다.

더불어민주당 홍의락 의원이 광해관리공단에서 제출받은
역에서 중금속 오염을 유발하는 폐광산은 모두 55곳으로

스포츠경향 주간경향 레이디경향 ENGLISH 로그인 회원가입 지면보기 구독신청

경향신문 지역

최신 지역일반 서울·수도권 충청 강원 영남 호남 제주 '코로나19' 속보

"봉화 영풍석포제련소 인근 토양 정화 수준 밝혀야"…환경단체 법률대응단, 정보공개 거듭 촉구

백경열 기자 merci@kyunghyang.com

입력 : 2019.09.19 16:59

경북 봉화군 석포면 영풍석포제련소 제1공장의 모습. | 백경열 기자 merci@kyunghyang.com

경북 봉화 영풍석포제련소의 환경오염 논란과 관련해 인근 땅의 정화 수준을 공개하라는 내용의 소송이 제기됐다.

영남 지역 환경단체가 연대한 '영풍석포제련소 공동대책위원회'의 법률대응단은 지난 10일 봉화군을

종합 많이 본 기사

1 [속보]청도 대남병원 코로나19 확진자 1명 사망…'폐렴 60대 환자' 사후 검사서 확인
2 코로나19 확진자 52명 추가 국내 총 156명…39명 신천지 대구교회 연관
3 [속보] 코로나19 확진자 22명 추가…국내 104명 발생
4 경남서도 첫 코로나19 확진자 발생
5 [속보]전 남편 살해 고유정 1심서 무기징역…의붓아들 살해는 무죄

오늘의 인기정보

오염토양의 원인자 추적 및 기여도 평가 활용

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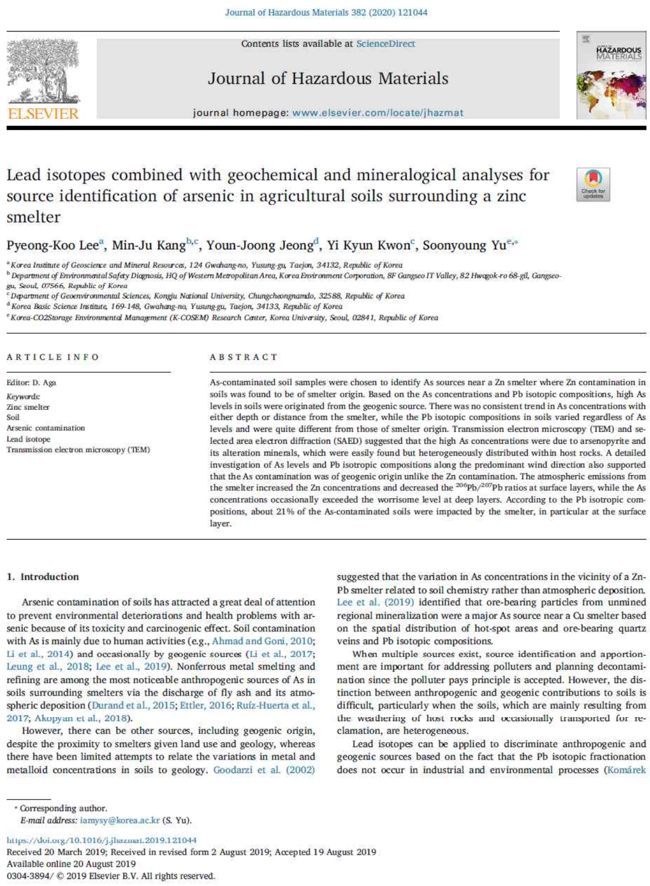

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Lead isotopes combined with geochemical and mineralogical analyses for source identification of arsenic in agricultural soils surrounding a zinc smelter

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ABSTRACT

As-contaminated soil samples were chosen to identify As sources near a Zn smelter where Zn contamination in soils was found to be of smelter origin. Based on the As concentrations and Pb isotopic compositions, high As levels in soils were originated from the geogenic source. There was no consistent trend in As concentrations with either depth or distance from the smelter, while the Pb isotopic compositions in soils varied regardless of As levels and were quite different from those of smelter origin. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) suggested that the high As concentrations were due to arsenopyrite and its alteration minerals, which were easily found but heterogeneously distributed within host rocks. A detailed investigation of As levels and Pb isotropic compositions along the predominant wind direction also supported that the As contamination was of geogenic origin unlike the Zn contamination. The atmospheric emissions from the smelter increased the Zn concentrations and decreased the $^{206}Pb/^{207}Pb$ ratios at surface layers, while the As concentrations occasionally exceeded the worrisome level at deep layers. According to the Pb isotropic compositions, about 21% of the As-contaminated soils were impacted by the smelter, in particular at the surface layer.

1. Introduction

Arsenic contamination of soils has attracted a great deal of attention to prevent environmental deteriorations and health problems with arsenic because of its toxicity and carcinogenic effect. Soil contamination with As is mainly due to human activities (e.g., Ahmad and Goni, 2010; Li et al., 2014) and occasionally by geogenic sources (Li et al., 2017; Leung et al., 2018; Lee et al., 2019). Nonferrous metal smelting and refining are among the most noticeable anthropogenic sources of As in soils surrounding smelters via the discharge of fly ash and its atmospheric deposition (Durand et al., 2015; Ettler, 2016; Ruíz-Huerta et al., 2017; Akopyan et al., 2018).

However, there can be other sources, including geogenic origin, despite the proximity to smelters given land use and geology, whereas there have been limited attempts to relate the variations in metal and metalloid concentrations in soils to geology. Goodarzi et al. (2002) suggested that the variation in As concentrations in the vicinity of a Zn-Pb smelter related to soil chemistry rather than atmospheric deposition. Lee et al. (2019) identified that ore-bearing particles from unmined regional mineralization were a major As source near a Cu smelter based on the spatial distribution of hot-spot areas and ore-bearing quartz veins and Pb isotopic compositions.

When multiple sources exist, source identification and apportionment are important for addressing polluters and planning decontamination since the polluter pays principle is accepted. However, the distinction between anthropogenic and geogenic contributions to soils is difficult, particularly when the soils, which are mainly resulting from the weathering of host rocks and occasionally transported for reclamation, are heterogeneous.

Lead isotopes can be applied to discriminate anthropogenic and geogenic sources based on the fact that the Pb isotopic fractionation does not occur in industrial and environmental processes (Komárek

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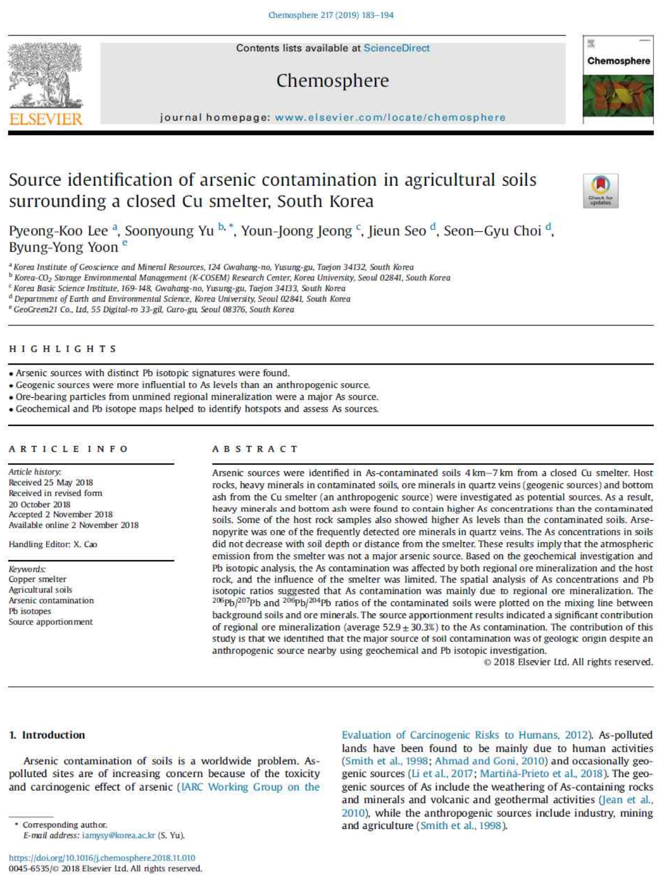

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Source identification of arsenic contamination in agricultural soils surrounding a closed Cu smelter, South Korea

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HIGHLIGHTS

- Arsenic sources with distinct Pb isotopic signatures were found.
- Geogenic sources were more influential to As levels than an anthropogenic source.
- Ore-bearing particles from unmined regional mineralization were a major As source.
- Geochemical and Pb isotope maps helped to identify hotspots and assess As sources.

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ABSTRACT

Arsenic sources were identified in As-contaminated soils 4 km–7 km from a closed Cu smelter. Host rocks, heavy minerals in contaminated soils, ore minerals in quartz veins (geogenic sources) and bottom ash from the Cu smelter (an anthropogenic source) were investigated as potential sources. As a result, heavy minerals and bottom ash were found to contain higher As concentrations than the contaminated soils. Some of the host rock samples also showed higher As levels than the contaminated soils. Arsenopyrite was one of the frequently detected ore minerals in quartz veins. The As concentrations in soils did not decrease with soil depth or distance from the smelter. These results imply that the atmospheric emission from the smelter was not a major arsenic source. Based on the geochemical investigation and Pb isotopic analysis, the As contamination was affected by both regional ore mineralization and the host rock, and the influence of the smelter was limited. The spatial analysis of As concentrations and Pb isotopic ratios suggested that As contamination was mainly due to regional ore mineralization. The $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ ratios of the contaminated soils were plotted on the mixing line between background soils and ore minerals. The source apportionment results indicated a significant contribution of regional ore mineralization (average 52.9 ± 30.3%) to the As contamination. The contribution of this study is that we identified that the major source of soil contamination was of geologic origin despite an anthropogenic source nearby using geochemical and Pb isotopic investigation.

1. Introduction

Arsenic contamination of soils is a worldwide problem. As-polluted sites are of increasing concern because of the toxicity and carcinogenic effect of arsenic (IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, 2012). As-polluted lands have been found to be mainly due to human activities (Smith et al., 1998; Ahmad and Goni, 2010) and occasionally geogenic sources (Li et al., 2017; Martiñá-Prieto et al., 2018). The geogenic sources of As include the weathering of As-containing rocks and minerals and volcanic and geothermal activities (Jean et al., 2010), while the anthropogenic sources include industry, mining and agriculture (Smith et al., 1998).

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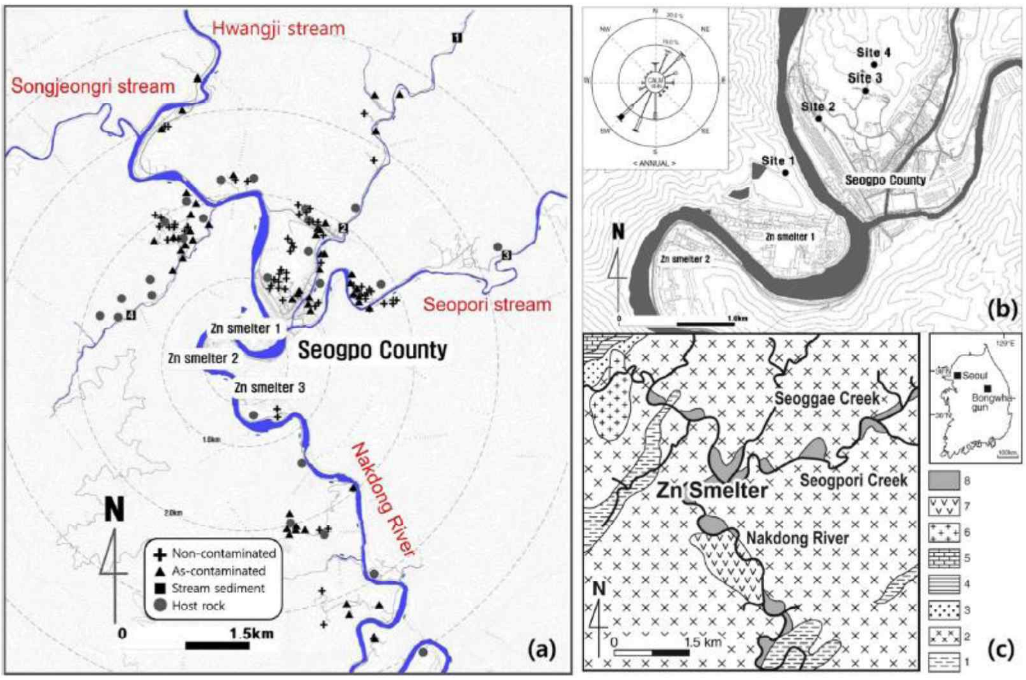

Fig. 1. (a) Sampling locations for non-contaminated soils (n = 76), As-contaminated soils (n = 66), host rocks (n = 27) and stream sediments (n = 4). (b) Sampling locations for additional 4 soil core samples (sites 1–4) along the main wind direction. (c) Geology of the study area. The lithologic units 1, 2, 3, 4, 5, 6, 7 and 8 represent Precambrian metasedimentary rocks, Precambrian Hongjesa granite gneiss, Cambrian Pungchon limestone, Cambrian Mobong slate, Cambrian Jangsan quartzite, Cretaceous granodiorite, Cretaceous volcanic rocks and alluvial deposits, respectively (after Korea Institute of Geoscience and Material Resources KIGAM, 1976; Kang et al., 2019).

오염토양의 원인자 추적 및 기여도 평가 활용

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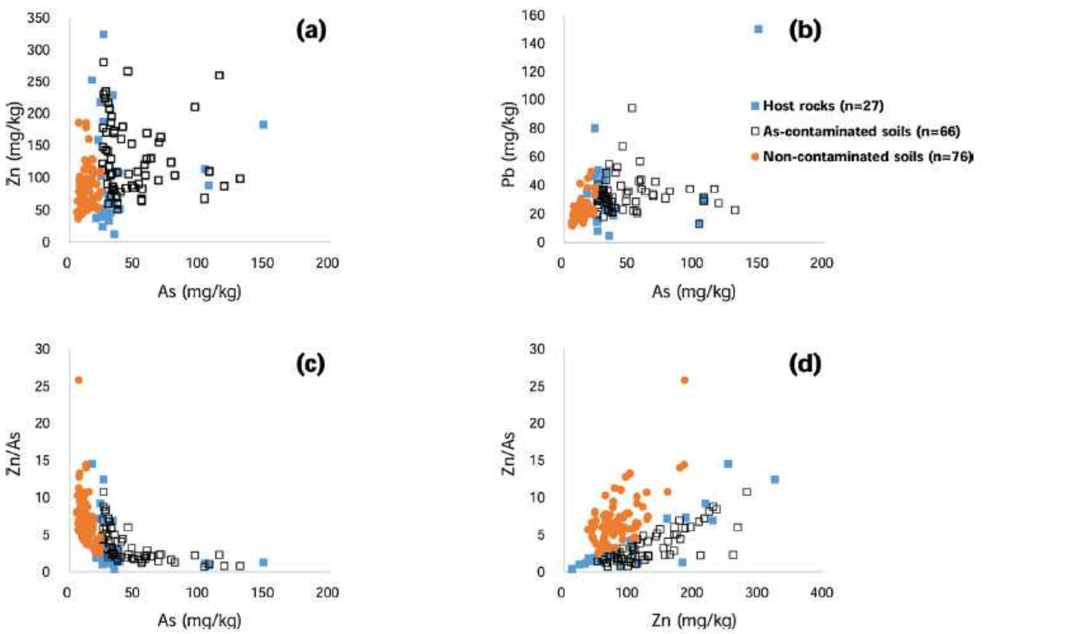

Fig. 2. As concentrations versus Zn concentrations (a) and Pb concentrations (b) in host rocks and soils. Zn/As versus As concentrations (c) and Zn concentrations (d). The As-contaminated and non-contaminated soils were grouped based on the Korean worrisome level (WL) for As (25 mg/kg). Note that all soil samples had Zn levels below 300 mg/kg (the Korean WL for Zn).

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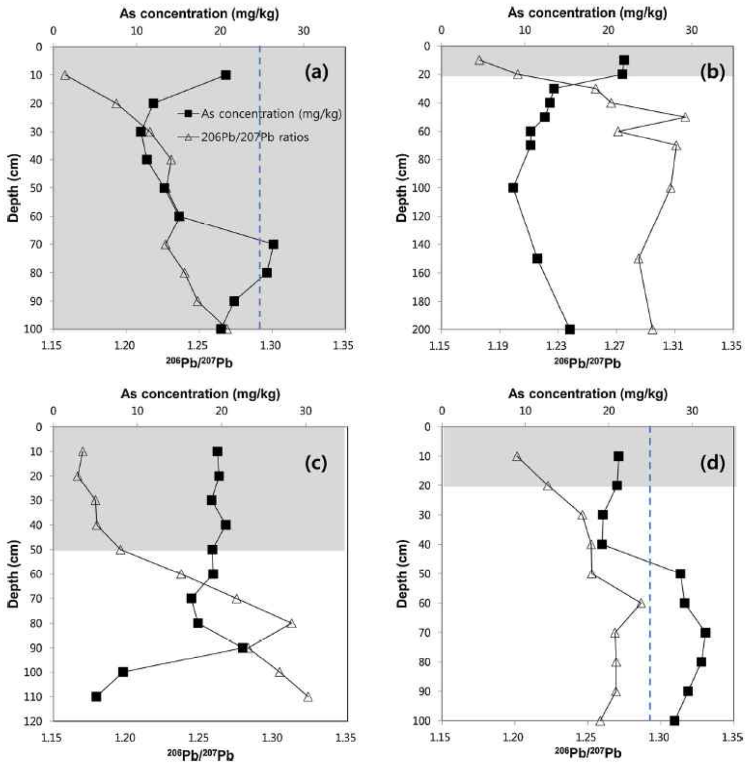

Fig. 4. The vertical distribution of As concentrations and $^{206}Pb/^{207}Pb$ ratios in the 4 soil core samples in Fig. 1b: (a) Site 1, (b) Site 2, (c) Site 3 and (d) Site 4. The dotted vertical lines indicate the Korean worrisome level (WL) for As (25 mg/kg). The shaded areas indicate the depths where the Zn levels were higher than the WL for Zn (300 mg/kg).

오염토양의 원인자 추적 및 기여도 평가 활용

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$$Pb(\%)_{anthropogenic} = \frac{(206Pb/^{207}Pb)_{geogenic} - (206Pb/^{207}Pb)_{sample}}{(206Pb/^{207}Pb)_{geogenic} - (206Pb/^{207}Pb)_{anthropogenic}} * 100$$

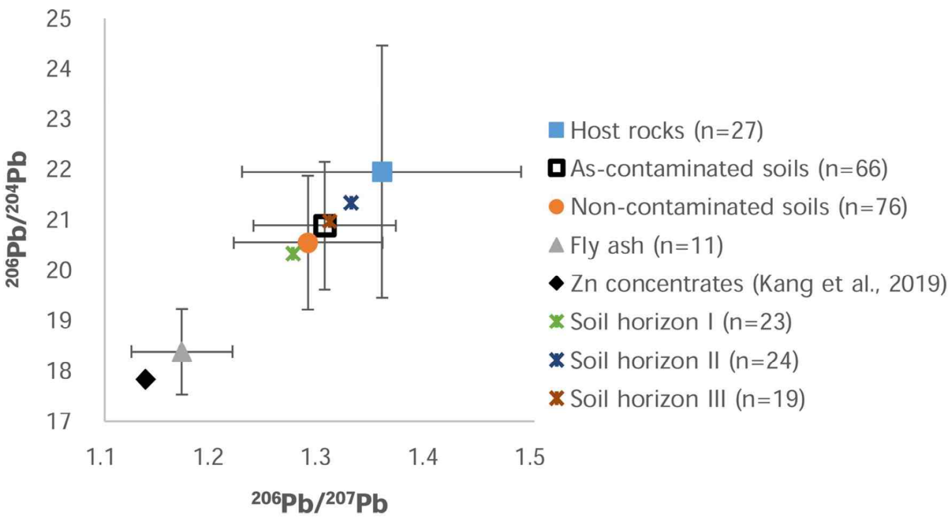

Fig. 5. Average $^{206}Pb/^{204}Pb$ ratios vs. $^{206}Pb/^{207}Pb$ ratios of host rocks, As-contaminated and non-contaminated soils, fly ash and Zn concentrates. The 66 As-contaminated soils were divided into three soil horizons I to III. The sold lines represent the standard deviations.

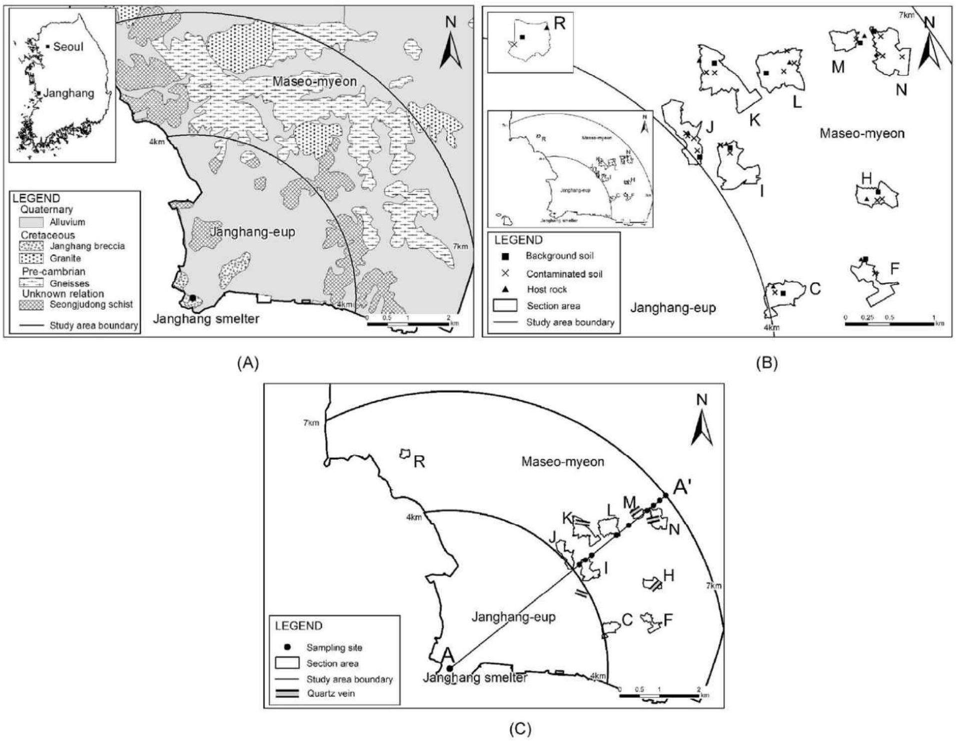

Fig. 1. (A) Geology of the study area. The lithologic units in (A) represent Precambrian metamorphic rocks and Cretaceous granite and Janghang breccia (after KIGAM, 1963). (B) Shows the sampling sites for background soil (n = 23), contaminated soil (n = 81) and host rock (n = 10) in 10 zones. Each zone had 2 or 3 background soil samples. The number of contaminated soil samples from Zones C, F, H, I, J, K, L, M, N, R was 4, 4, 9, 5, 16, 8, 10, 5, 16 and 4, respectively. Host rock samples were collected at outcrops close to where the cores for background soil samples were collected. (C) A-A' line following the prevailing wind direction in this study area.

오염토양의 원인자 추적 및 기여도 평가 활용

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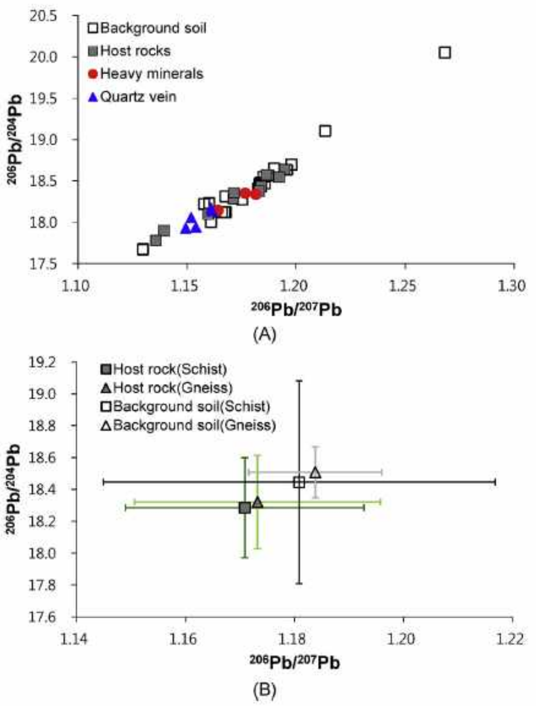

Fig. 2. (A) $^{206}Pb/^{207}Pb$ versus $^{206}Pb/^{204}Pb$ of background soil (n = 23), host rock (n = 10), heavy minerals extracted from the contaminated soil (n = 3) and ore minerals of quartz veins (n = 7). (B) Average $^{206}Pb/^{207}Pb$ versus $^{206}Pb/^{204}Pb$ based on the geology. 10 cores for background soil samples and 10 host rock samples were collected from schist (n = 6) and gneiss (n = 4), respectively.

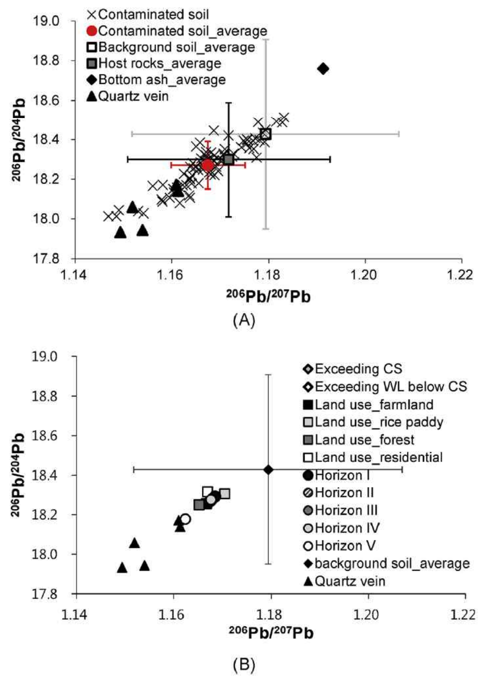

Fig. 3. (A) $^{206}Pb/^{207}Pb$ versus $^{206}Pb/^{204}Pb$ of contaminated soil samples (n = 81). For comparison, the average $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ ratios for the contaminated soil (n = 81), background soil (n = 23), host rock (n = 10), bottom ash from the Cu smelter (n = 2) and ore minerals of quartz veins (n = 7) were also shown. (B) Average $^{206}Pb/^{207}Pb$ versus $^{206}Pb/^{204}Pb$ of contaminated soil samples (n = 81) grouped by concentration level (CS, WL), sampling depth (Horizon I to V), land use (farmland, paddy field, forest and residential area). Note that the values classified by concentration level, sampling depth and land use were similar to each other, and thus their symbols are overlapped and not distinct in Fig. 3B.

오염토양의 원인자 추적 및 기여도 평가 활용

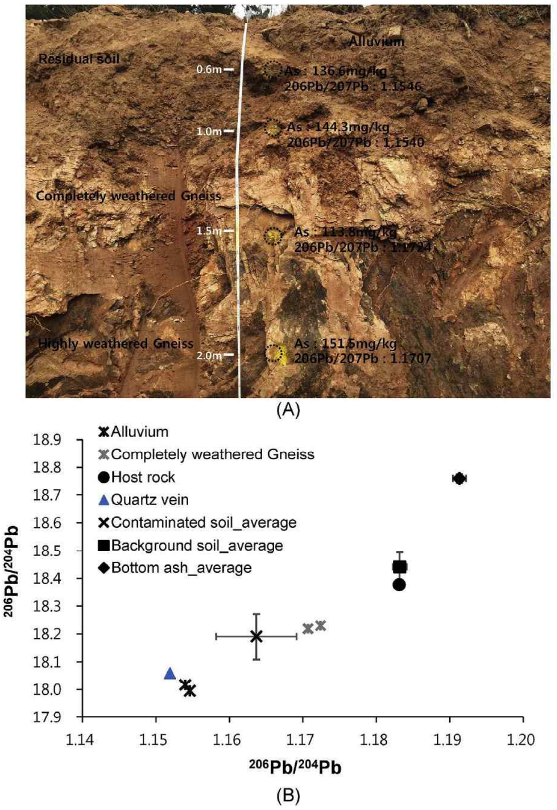

Fig. 4. (A) Vertical variation of As concentrations and $^{206}Pb/^{207}Pb$ isotopic ratios in soil profile observed in Zone N. Quartz vein was observed on the other side of this outcrop. (B) $^{206}Pb/^{207}Pb$ versus $^{206}Pb/^{204}Pb$ of alluvium (n = 2) and completely weathered gneiss (n = 2) in Zone N. For comparison, the average $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ ratios of contaminated soil samples (n = 16), background soil (n = 2), host rock (n = 1) and ore mineral of quartz vein in Zone N and bottom ash from the Cu smelter (n = 2) were also shown.

오염토양의 원인자 추적 및 기여도 평가 활용

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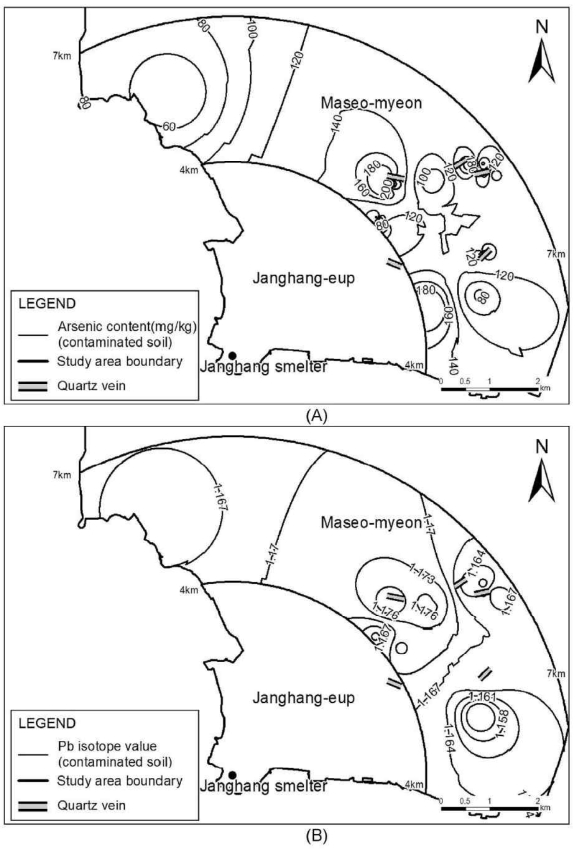
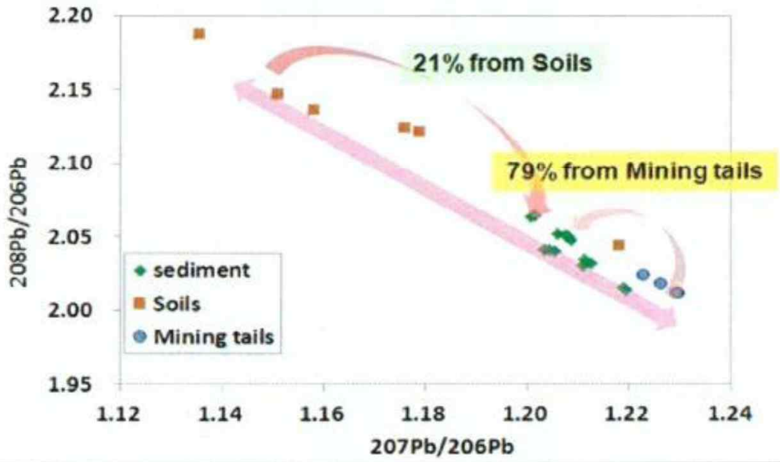


Fig. 5. Contour maps in Horizon I (0–30 cm): (A) As concentration and (B) $^{206}Pb/^{207}Pb$ isotopic ratio. For comparison, ore-bearing quartz veins were also shown.

오염토양의 원인자 추적 및 기여도 평가 활용



<그림 5-1> 안동댐 퇴적물 오염 기여도 배분

김영희 등 (2012) 국립환경과학원

황사 및 미세먼지의 원인자 추적

한국기초과학지원연구원
KOREA BASIC SCIENCE INSTITUTE

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Lead isotopes combined with a sequential extraction procedure for source apportionment in the dry deposition of Asian dust and non-Asian dust

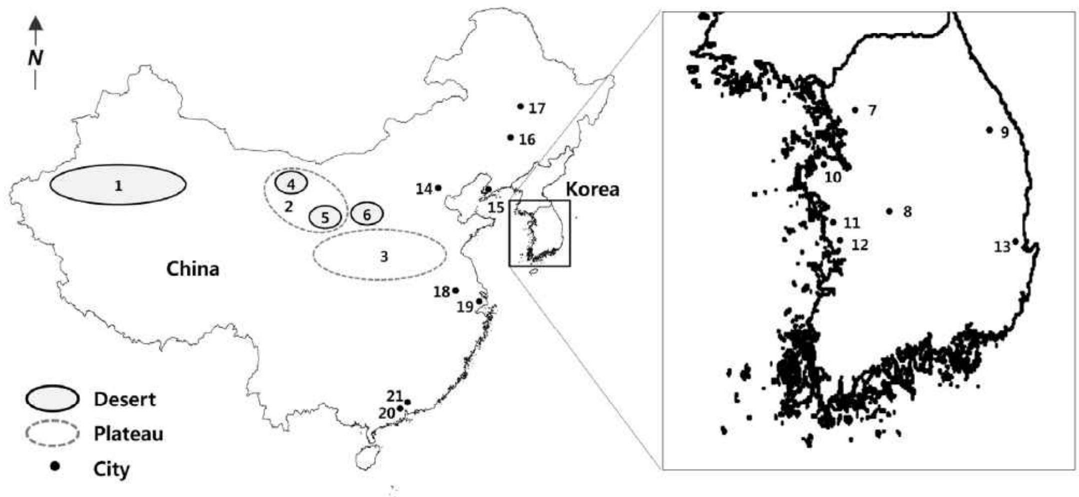

Fig. 1. Location map of sampling sites (not to scale). 1) Taklamakan desert; 2) Alashan Plateau; 3) Loess Plateau; 4) Badain Jaran desert; 5) Tengger desert; 6) Ordos desert; 7) Seoul; 8) Daejeon; 9) Taeback; 10) Dangjin; 11) Boryeong; 12) Seocheon; 13) Pohang; 14) Beijing; 15) Dalian; 16) Changchun; 17) Harbin; 18) Nanjing; 19) Shanghai; 20) Foshan; 21) Guanzhou. The solid box enlarges the South Korea.

황사 및 미세먼지의 원인자 추적

- A five-step sequential extraction was performed using 0.2~1g.

- Exchangeable fraction (F1) : *exchangeable*
- Carbonate fraction (F2) : *bound to carbonate minerals*
- Reducible fraction (F3) : *bound to amorphous Fe and Mn hydroxides*
- Organic and sulfide fraction (F4) : *bound to organic matter and sulfide minerals*
- Residual fraction (F5) : *residual*

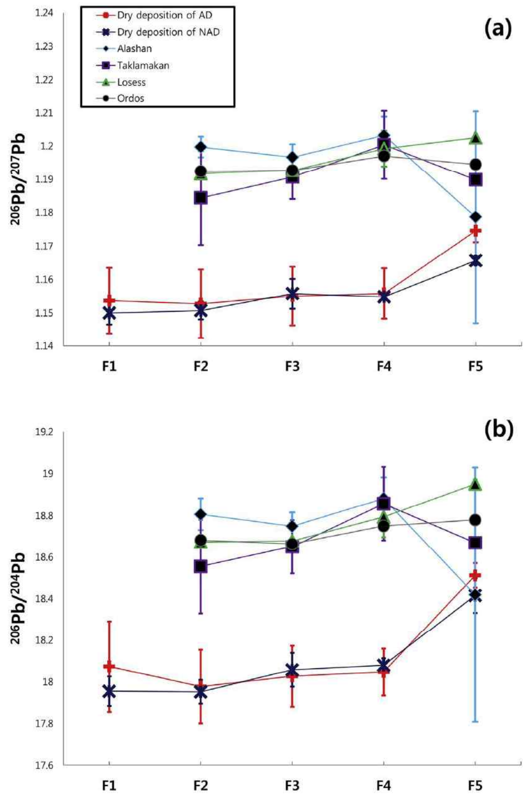

Fig. 3. Average Pb isotopic compositions in the five fractions of the dry deposition of AD and NAD and in the four fractions of Chinese desert soils. (a) $^{206}Pb/^{207}Pb$; (b) $^{206}Pb/^{204}Pb$. The error bars represent the standard deviation of the measurements.

미립자에 대한 in-situ 동위원소 분석

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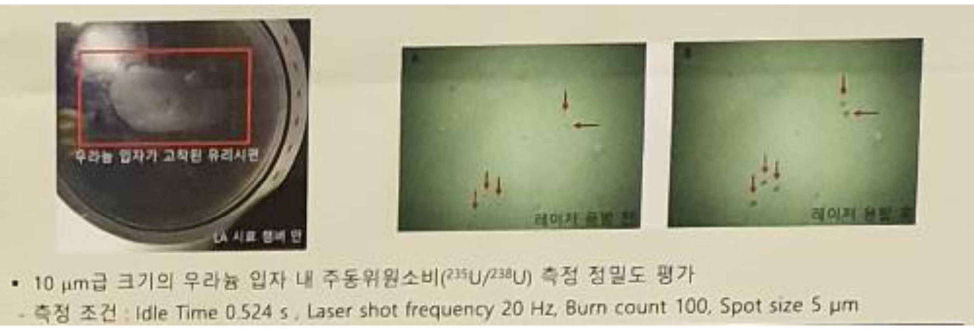
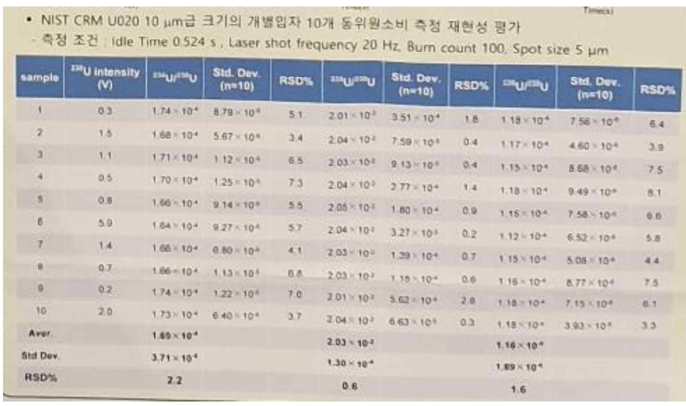
fs-LA-MC-ICPMS를 이용한 um급 크기의 우라늄 입자 동위원소비 분석



NIST CRM U020 10um급 크기의 개별입자 10개의 우라늄 동위원소비 분석



- NIST CRM U020 10 μm급 크기의 개별입자 10개 동위원소비 측정 재현성 평가
  - 측정 조건 : Idle Time 0.524 s , Laser shot frequency 20 Hz, Burn count 100, Spot size 5 μm

sample	^{238}U intensity (V)	$^{234}U/^{238}U$	Std. Dev. (n=10)	RSD%	$^{235}U/^{238}U$	Std. Dev. (n=10)	RSD%	$^{236}U/^{238}U$	Std. Dev. (n=10)	RSD%
1	0.3	1.74×10^{-4}	8.79×10^{-6}	5.1	2.01×10^{-2}	3.51×10^{-4}	1.8	1.18×10^{-4}	7.56×10^{-6}	6.4
2	1.5	1.68×10^{-4}	5.67×10^{-6}	3.4	2.04×10^{-2}	7.59×10^{-5}	0.4	1.17×10^{-4}	4.60×10^{-6}	3.9
3	1.1	1.71×10^{-4}	1.12×10^{-5}	6.5	2.03×10^{-2}	9.13×10^{-5}	0.4	1.15×10^{-4}	8.68×10^{-6}	7.5
4	0.5	1.70×10^{-4}	1.25×10^{-5}	7.3	2.04×10^{-2}	2.77×10^{-4}	1.4	1.18×10^{-4}	9.49×10^{-6}	8.1
5	0.8	1.66×10^{-4}	9.14×10^{-6}	5.5	2.05×10^{-2}	1.80×10^{-4}	0.9	1.15×10^{-4}	7.58×10^{-6}	6.6
6	5.9	1.64×10^{-4}	9.27×10^{-6}	5.7	2.04×10^{-2}	3.27×10^{-5}	0.2	1.12×10^{-4}	6.52×10^{-6}	5.8
7	1.4	1.66×10^{-4}	6.80×10^{-6}	4.1	2.03×10^{-2}	1.39×10^{-4}	0.7	1.15×10^{-4}	5.08×10^{-6}	4.4
8	0.7	1.66×10^{-4}	1.13×10^{-5}	6.8	2.03×10^{-2}	1.15×10^{-4}	0.6	1.16×10^{-4}	8.77×10^{-6}	7.5
9	0.2	1.74×10^{-4}	1.22×10^{-5}	7.0	2.01×10^{-2}	5.62×10^{-4}	2.8	1.18×10^{-4}	7.15×10^{-6}	6.1
10	2.0	1.73×10^{-4}	6.40×10^{-6}	3.7	2.04×10^{-2}	6.63×10^{-5}	0.3	1.18×10^{-4}	3.93×10^{-6}	3.3
Aver.		**1.69×10^{-4}**			**2.03×10^{-2}**			**1.16×10^{-4}**		
Std Dev.		**3.71×10^{-6}**			**1.30×10^{-4}**			**1.89×10^{-6}**		
RSD%		**2.2**			**0.6**			**1.6**		

LA-MC-ICPMS

Laser ablation multi-collectors inductively coupled plasma mass spectrometer
(레이저 삭박 다검출기 유도결합 이온플라즈마 질량분석기)

NWR193^{UC} with Nu Plasma II in KBSI

LA-MC-ICPMS를 이용한 입자 분석

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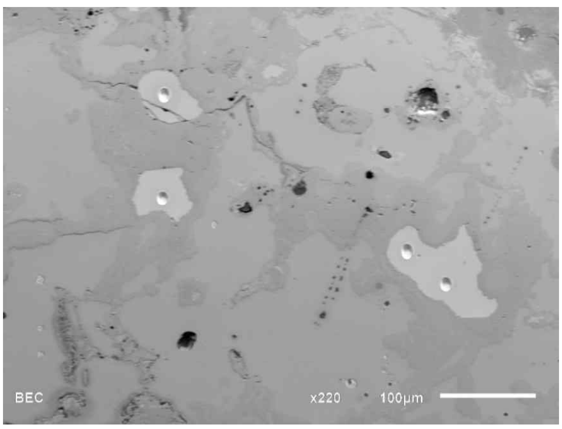

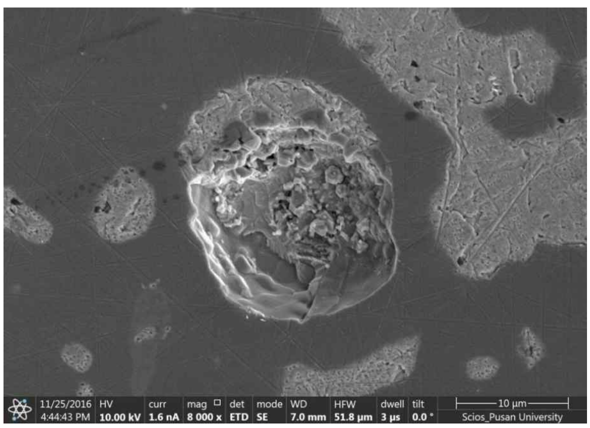

Spot size : 10um
Laser fluence : 0.13J/cm^2

과학으로 지키는 국민행복, with KBSI!

Thank You

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