Chapter 3

Chemistry and Mineralogy of Igneous Rocks

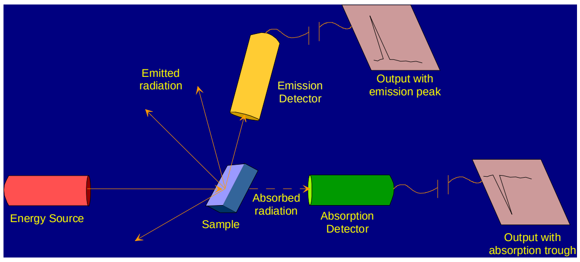
지구, 맨틀, 지각의 화학 조성 (wt.%)

Element	Earth [a]	Oxide	Mantle [a]	Oceanic crust [b]	Continental crust [c]
Fe	31	SiO_2	45.2	49.4	60.3
O	30	TiO_2	0.71	1.4	1.0
Si	18	Al_2O_3	3.54	15.4	15.6
Mg	16	FeO_{total}	8.48	10.1	7.2
Ni	1.7	MnO	0.14	0.3	0.1
Ca	1.8	MgO	37.48	7.6	3.9
Al	1.4	CaO	3.08	12.5	5.8
Na	0.9	Na_2O	0.57	2.6	3.2
		K_2O	0.13	0.3	2.5
		P_2O_5	-	0.2	0.2

a. Ringwood, 1975, *Composition and Petrology of the Earth's Mantle*. New York: McGraw-Hill
b. Ronov and Yarovshevsky, 1969, *Chemical Composition of the Earth's Crust*. American Geophysical Union Monograph 13.
c. Taylor, 1964, Abundance of cehmical elements in the continental crust: a new table. *Geochim. Cosmochim. Acta 28*. 1273-1285.

- 주원소 (Major element): >1 wt.% (oxide)
  - SiO_2, Al_2O_3, FeO, MgO, CaO, Na_2O, K_2O
- 미량원소 (Minor element)
  - TiO_2, MnO, P_2O_5, volatiles(H_2O, CO_2)
  - 특정 광물로 존재하는 경우도 있음
- 흔적원소 (Trace element)
  - 특정 광물로 존재하기 힘듦(간혹 존재 ex. Monazite, allanite 등)
  - 희토류원소 (Rare earth element)
- 동위원소 (Isotope)

현대식 분광 분석 기술
(Ex. XRF, EPMA, ICP, TIMS, SIMS etc)



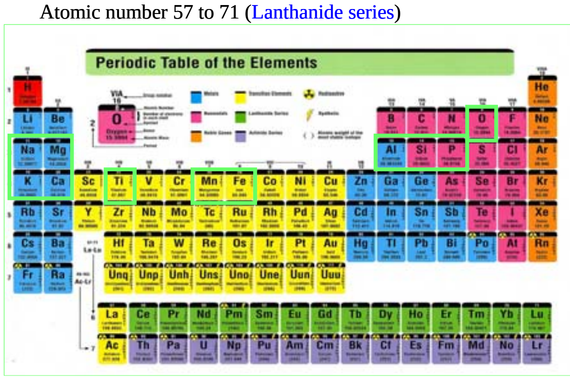
The geometry of typical spectroscopic instruments. From Winter (2001) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall.

실제 분석

- 주원소+미량원소 분석: >0.1 wt.% (oxide)
  - 암석 분말 시료: X-선 형광분석(XRF) or 습식 분석
  - SiO_2, Al_2O_3, FeO, MgO, CaO, Na_2O, K_2O, TiO_2, MnO, P_2O_5
- 흔적원소 + 동위원소
  - 암석 분말 시료나 광물 시료를 특별한 전처리를 통해서 질량분석기나 분광기류로 분석 가능 (ICP, SHRIMP, TIMS etc)

Major Elements (주원소)

Atomic number 57 to 71 (Lanthanide series)



화성암의 지구화학

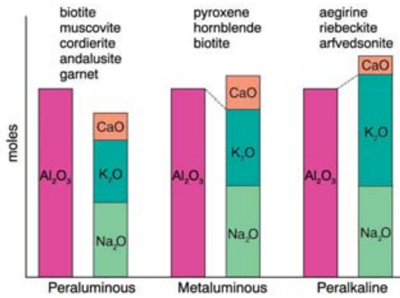
- **주원소**, 미량원소 , 흔적원소
- 주원소: O, Si, Al, Fe, Ca, Na, Mg, K, Ti, H, P, Mn (간혹 C, S)
  - **산화물 형태**
  - **단위 : Weight percent** (wt.%)
  - Si와 Na, K는 **비례**
  - Si와 Fe, Mg, Ca는 **반비례**
  - SiO_2 함량은 암석 구분의 척도로 이용
  - SiO_2, Al_2O_3 함량은 화성암의 광물 성분 조절
    - Ex. SiO2 포화(장석+석영)/불포화(준장석)

Table 3.1. Chemical analysis of Typical Igneous Rocks

	Dunite	Basalt	Andesite	Syenite	Granite	Rhyolite
SiO_2	40.08	49.8	58.97	59.54	69.22	77.24
TiO_2	0.01	2.6	1.04	0.14	0.48	0.2
Al_2O_3	0.29	14	17.17	18.6	15.5	1.81
Fe_2O_3	0.31	2.5	4.36	2.86	1.03	1.66
FeO	7.62	8.5	2.02	2.09	1.42	0.27
MnO	0.11	0.18	0.1	0.22	0.04	0.02
MgO	49.69	7.2	1.51	0.1	0.73	0.33
CaO	0.11	11.3	4.9	1.16	1.93	1.48
Na_2O	0.05	2.2	4.23	8.96	4.15	2.59
K_2O	0.01	0.62	2.9	4.24	4.42	4.12
P_2O_5	0	0.32	0.51	0.16	0.15	0.06
H_2O^+		0.25		1.4		0.37
Other	0.58	0.1	1.55	0.4	0.3	0.65
Total	98.86	99.6	99.26	99.87	99.37	99.8

알루미나 포화

분류



$Al_2O_3/(CaO+Na_2O+K_2O)$
(A/CNK)
몰 분률 이용
(after Shand ,1927).

과알루미나형(peraluminous) : Al2O3 > CaO+K2O+Na2O
중알루미나형(metaluminous) : K2O+Na2O < Al2O3
< CaO+K2O+Na2O
저알루미나형(subaluminous) : Al2O3 = CaO+K2O+Na2O
고알칼리형 (peralkaline) : Al2O3 < K2O+Na2O
Major element 의 diagram : Fig. 3.2, 3, 4 참조(2성분, 3성분 diagram)

하와이 화산암에 대한 Alkali vs. Silica diagram

alkaline과 subalkaline 뚜렷한 두개의 그룹이 존재

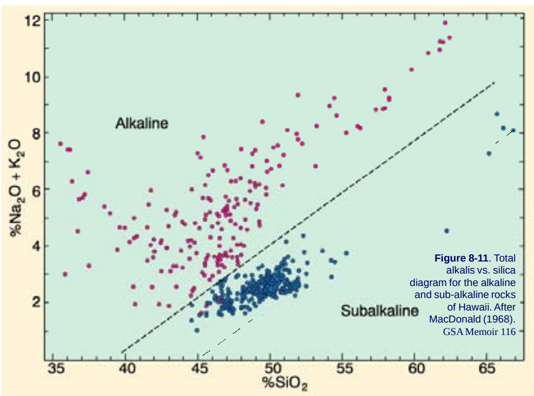
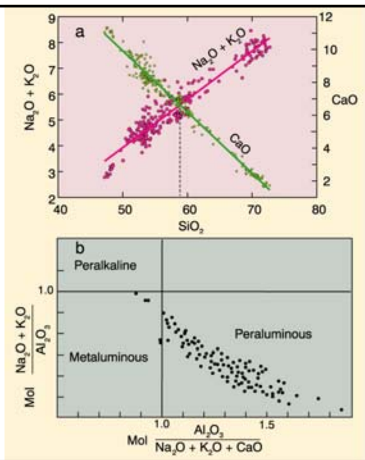


Figure 8-11. Total alkalis vs. silica diagram for the alkaline and sub-alkaline rocks of Hawaii. After MacDonald (1968). GSA Memoir 116

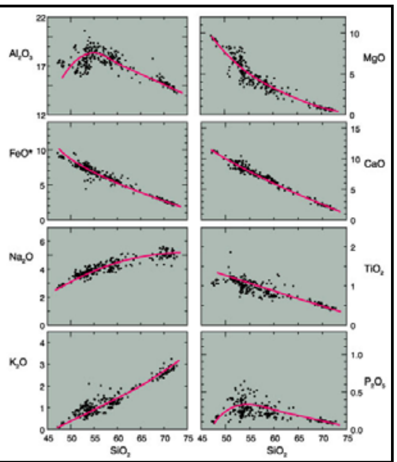
Figure 8-10a. Peacock (1931) used the value of SiO_2 at which the two curves crossed as his "alkali-lime index" (dashed line). b. Alumina saturation indices (Shand, 1927) with analyses of the peraluminous granitic rocks from the Achala Batholith, Argentina (Lira and Kirschbaum, 1990). In S. M. Kay and C. W. Rapela (eds.), Plutonism from Antarctica to Alaska. Geol. Soc. Amer. Special Paper, 241. pp. 67-76.

Crater Lake data의 CaO (green) 및 $(Na_2O + K_2O)$ (red) vs. SiO_2 diagram.



Bivariate (x-y) diagrams

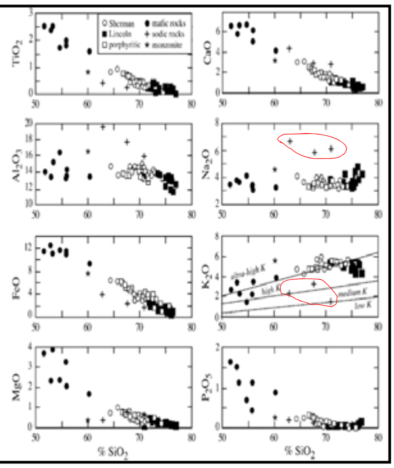
Harker's diagram :
SiO2 vs. other elements



Harker variation diagram for 310 analyzed volcanic rocks from Crater Lake (Mt. Mazama), Oregon Cascades. Data compiled by Rick Conrey (personal communication).

Bivariate (x-y) diagrams

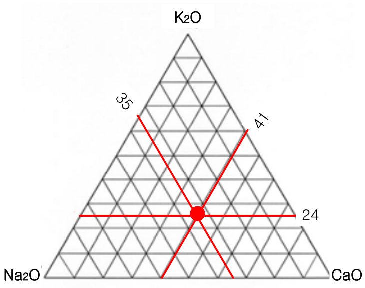
Harker diagram :
SiO2 vs. other elements
Magma type, origin
등을 판단하는 참고자료



Variation of major element contents of rocks from the Sherman batholith, SE Wyoming, USA.(Frost et al. 1999. J. Petrol.)

Triangular variation diagram (Example).

(wt.%)	Andesite	
SiO_2	58.97	
TiO_2	1.04	
Al_2O_3	17.17	
Fe_2O_3	4.36	
FeO	2.02	
MnO	0.1	
MgO	1.51	
CaO	4.9	41
Na_2O	4.23	35
K_2O	2.9	24
P_2O_5	0.51	
H_2O^+		
Other	1.55	
Total	99.26	

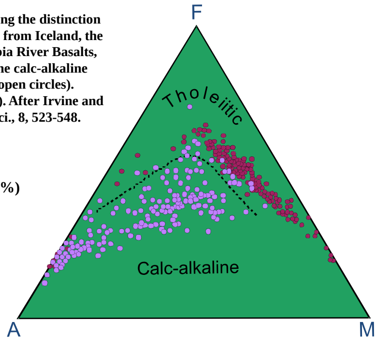


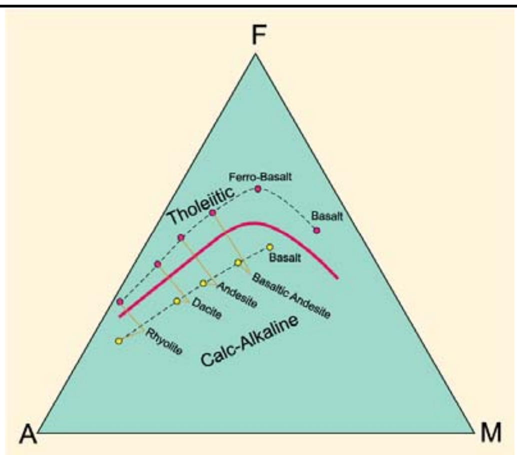
$$K_2O(wt.\%) = \frac{K_2O \times 100}{K_2O + Na_2O + CaO} = 24\%$$

Example of ternary diagram: AFM diagram: can further subdivide the subalkaline magma series into a tholeiitic and a calc-alkaline series

Figure 3-4. AFM diagram showing the distinction between selected tholeiitic rocks from Iceland, the Mid-Atlantic Ridge, the Columbia River Basalts, and Hawaii (solid circles) plus the calc-alkaline rocks of the Cascade volcanics (open circles). From Irving and Baragar (1971). After Irvine and Baragar (1971). Can. J. Earth Sci., 8, 523-548.

A = K2O + Na2O
F = FeO total (Fe_2O_3 + FeO)
M = MgO (wt.%)



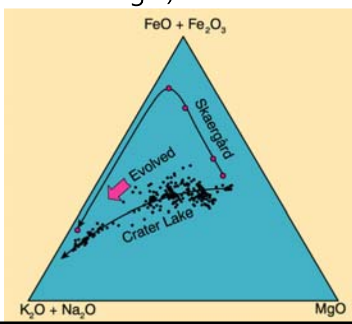


Ternary Variation Diagrams

Example: AFM diagram

(alkalis$_{(Na_2O+K_2O)}$-FeO$_{total}$-MgO)

AFM diagram for Crater Lake volcanics, Oregon Cascades. Data compiled by Rick Conrey (personal communication).

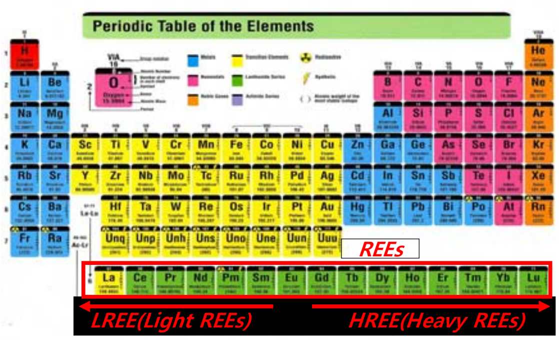


Trace elements (미량원소)

- 주원소를 제외한 나머지 모든 원소
- C, S, Cr은 다량 산출하는 경우도 있음.
- 단위 : ppm (parts per million), ppb (parts per billion)
  - Ex 1 ppm = 1 g/ton (10,000 ppm = 1 wt.%)
- Rare earth elements(REE), Isotope, other trace elements

Rare Earth Elements (REE)

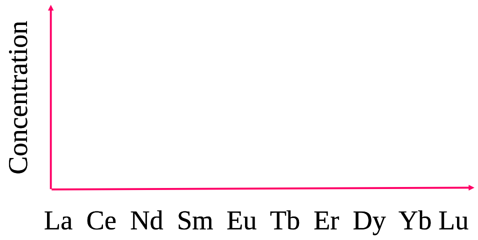
Atomic number 57 to 71 (Lanthanide series)

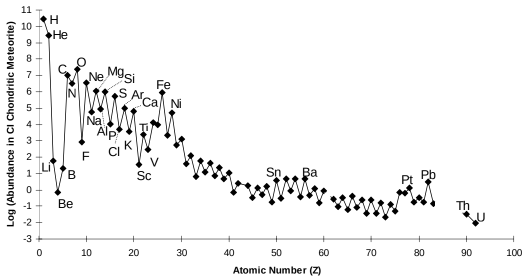


REE Diagrams

Plots of concentration as the ordinate (y-axis) against increasing atomic number (log scale)

Degree of compatibility increases from left to right across the diagram (x-axis)





- Eliminate Oddo-Harkins effect and make y-scale more functional by normalizing to a standard (짝수의 원자번호를 갖는 것이 상대적으로 양이 많은 현상)
  - chondrite meteorite concentrations (콘드라이트)
  - estimates of primordial mantle REE (원시 맨틀)
- Oddo-Harkins rule argues that elements with odd atomic numbers have one unpaired proton and are more likely to capture another

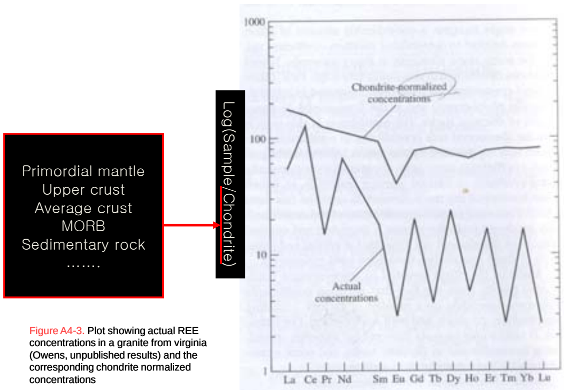
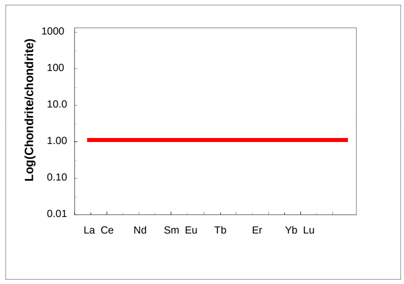


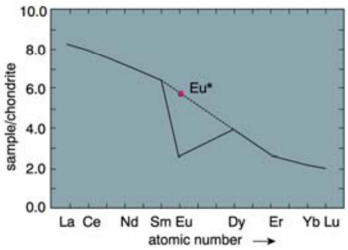
Figure A4-3. Plot showing actual REE concentrations in a granite from virginia (Owens, unpublished results) and the corresponding chondrite normalized concentrations

Chondrite(운석)를 분석해서 아래에 그려 넣으면?



Thus, this sample is chondrite.

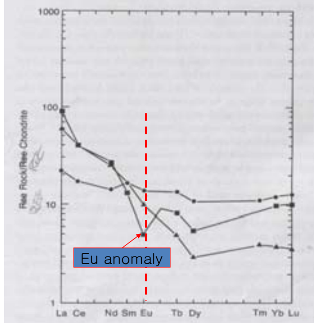
- Europium anomaly when plagioclase is
  - a fractionating phenocryst (plagioclase) or
  - a residual solid in source



Most REE do not substitute readily in minerals but Eu substitute Ca.

Figure 9-5. REE diagram for 10% batch melting of a hypothetical lherzolite with 20% plagioclase, resulting in a pronounced negative Europium anomaly. From Winter (2001) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall.

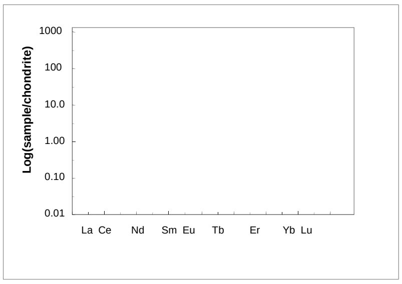
- REE 분석은 마그마 분화작용을 이해하는데 도움을 준다 (기울기, Eu 이상치 등).
- REE는 거의 비슷한 성질을 갖으나 일부 LREE, HREE, Eu에 따라서 광물에 선택적으로 들어가는 성질때문이다.



기울기, Eu 이상치는 좋은 지표가 됨.

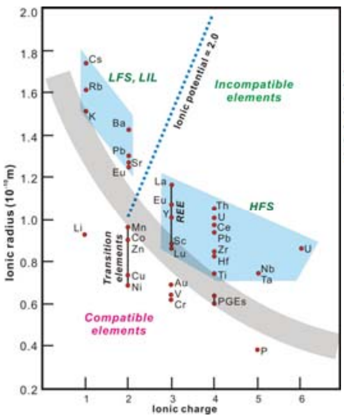
Figure 3.5. REE diagram showing curves for three common rock types. Circles = a plagioclase-rich granitoid rock. Triangles = granodiorites. Squares = a leucogranite showing Eu anomaly.

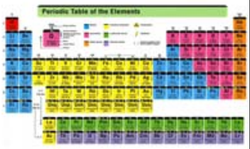
맨틀, 반려암, 섬록암, 화강암을 아래 다이어그램에 그려넣으면?



Compatible & Incompatible

- Incompatible element (불호정 원소; 不好晶) : 상대적으로 melt에 들어가기 좋아하는 원소
  - 대부분의 HFSE, LILE 가 모두 여기에 해당됨.
- Compatible element (호정 원소; 好晶) : 상대적으로 mineral (solid)에 들어가는 것을 좋아하는 원소

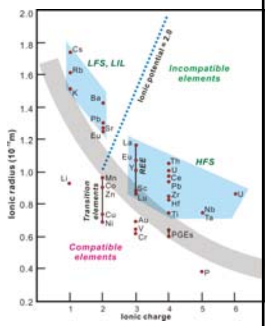




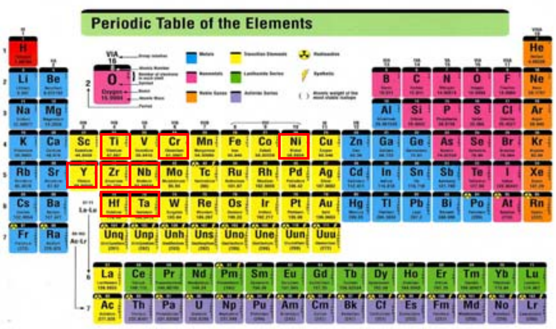
Plot of ionic radiius vs ionic charge for trace elements of geological interest. An ionic potential (charge/size ratio) of 2.0 subdivides the incompatible elements into low field strength (LFS) elements, also known as large ion lithophile elements (LIL) and high field strength elements (HFS). Compatible elements are placed towards the bottom, left-hand corner of diagram. The ionic radii are from Shannon (1976) and are quoted for eight-fold coordination to allow a comparison between elements. Some of the first transition series metals (transition elements) and the PGE element, are quoted for six-fold coordination. (Rollinson, 1993, Usion geochemical data. PEARSON)

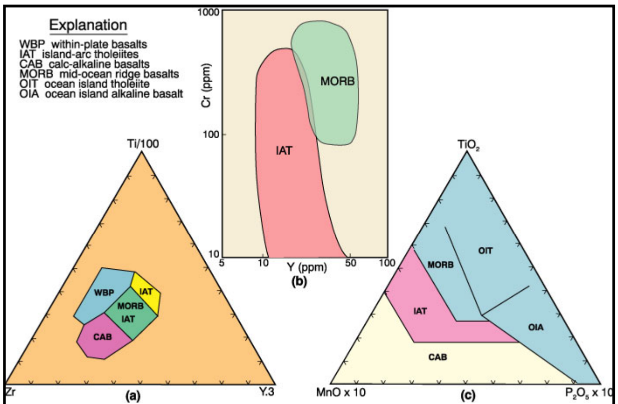
High field strength elements (HFSE; 고장력원소)

- Have high charge/radius ratio
- Ti, Ni, Cr, Zr, Hf, Nb, Ta, Y
- Incompatible element (불호정 원소)에 속함
- 여러 화성암 사이의 성인적 연관성을 반영
  - Ex. 동일한 비율을 갖는 magma와 dike
- 표현방식에 다양한 diagram을 사용
  - Divariant, ternary, 생성환경 다이어그램, spider diagram 등



HFSE

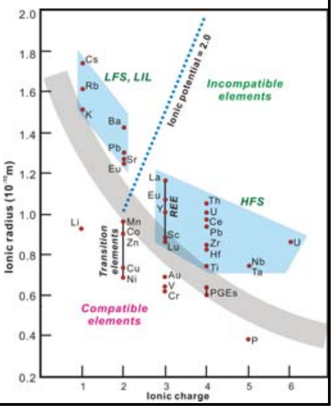




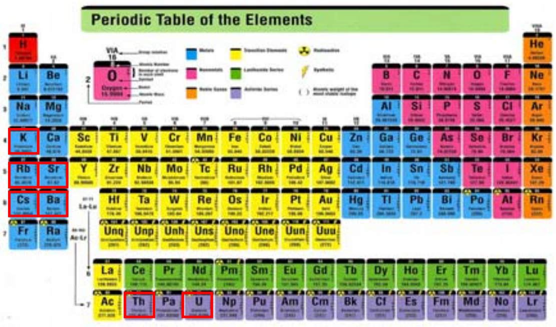
(a) after Pearce and Cann (1973), Earth Planet, Sci. Lett., **19**, 290-300. (b) after Pearce (1982) in Thorpe (ed.), Andesites: Orogenic andesites and related rocks. Wiley. Chichester. pp. 525-548, Coish et al. (1986), Amer. J. Sci., **286**, 1-28. (c) after Mullen (1983), Earth Planet. Sci. Lett., **62**, 53-62.

Large-ion lithophile (LIL) element 친석 원소

- 이온 반경은 크지만 ionic charge가 작은 원소 (incompatible elements) : 상대적으로 melt에 있기를 좋아함.
- K, Rb, Sr, Cs, Ba, Th, U



HFSE



스파이더 (Spider) 다이어그램

REE 원소 표현방식의 확장: 원소들의 대략적인 분포 경향성을 확인하는데 이용

콘드라이트 값으로 표준화한 스파이더 다이어그램 (다중원소 다이어그램) : 일반적으로 사용자의 판단에 따라 원소가 배열됨 (좌측으로 갈수록 불호정성 증가)

Different estimates → different ordering (poor standardization)

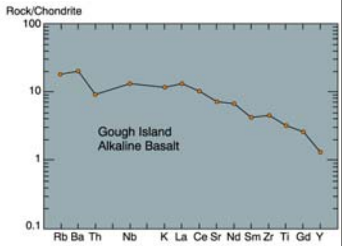


Fig. 9-6. Spider diagram for an alkaline basalt from Gough Island, southern Atlantic. After Sun and MacDonough (1989). In A. D. Saunders and M. J. Norry (eds.), Magmatism in the Ocean Basins. Geol. Soc. London Spec. Publ., **42**. pp. 313-345.

MORB-normalized Spider

Separates LIL and HFS (MORB = mid ocean ridge basalt)

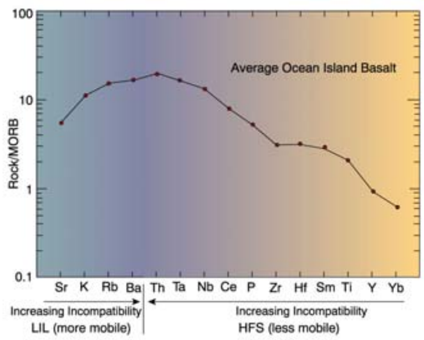
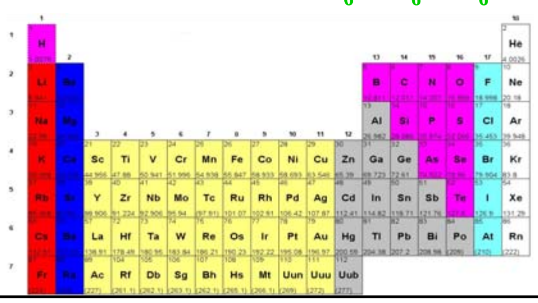


Figure 9-7. Ocean island basalt plotted on a mid-ocean ridge basalt (MORB) normalized spider diagram of the type used by Pearce (1983). Data from Sun and McDonough (1989). From Winter (2001) An Introduction to Igneous and Metamorphic Petrology. Prentice Hall.

Isotopes

Same atomic number, different atomic weight (variable # of neutrons)

General notation for a nuclide: ${}^{12}_{6}C$ ${}^{13}_{6}C$ ${}^{14}_{6}C$



Stable Isotopes

- Stable: last ~ forever
- 화학적인 구분은 불가능함
- 질량 분화만이 가능(질량분석기)
- 대표적인 안정동위원소 : H, O, C, S
- 특정 작용(환경) 추적에 이용.

^{16}O	99.756%	of natural oxygen
^{17}O	0.039%	"
^{18}O	0.205%	"

Radioactive Isotopes (방사성 동위원소)

- 다른 원자로 붕괴하는 불안정한 동위원소
- 주로 연대측정에 이용
- 붕괴 비율은 매우 일정하고 온도, 압력, 화학성분에 영향을 안받는다.
- Parent nuclide = radioactive nuclide that decays
- Daughter nuclide(s) are the radiogenic *atomic* products
- K/Ar, Ar/Ar, Rb/Sr, Nd/Sm, U/Pb, Pb/Pb