Geochemistry

GEODEEP 9300

LEA BELOŠA

3.11.2021

What is geochemistry?

- study of the Earth's chemical composition and chemical development

→ elemental distribution in time and space together with principles of chemistry → mechanisms behind major geological systems such as the Earth's crust and its oceans

* realm of geochemistry extends beyond the Earth, encompassing the entire Solar System (formation of planets)

1. chemical **processes and reactions** that govern the composition of rocks and soils (origins of granite and basalt)
2. the **cycles of matter and energy** that transport the Earth's chemical components (including mantle convection)
3. their **interaction** with the hydrosphere and atmosphere

Historical overview

1838 “geochemistry” - first used by the Swiss-German chemist **Christian Friedrich Schönbein**

- the rest of the century the more common term was "chemical geology“

-little contact between geologists and chemists

1884 United States Geological Survey (USGS)

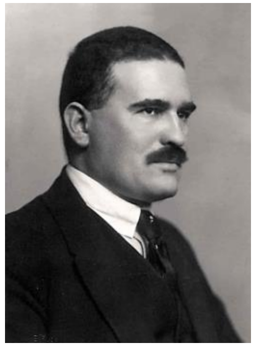
-geochemistry emerged as a separate discipline after major laboratories were established

1850 beginnings of the field of cosmochemistry

-composition of meteorites was investigated and compared to terrestrial rocks

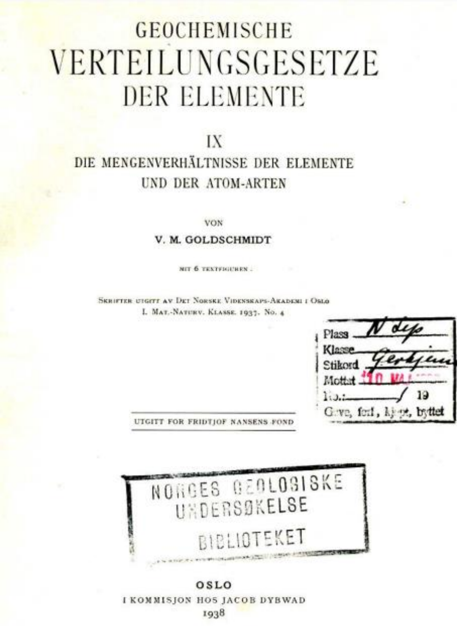
1920s and 1930s **Victor Goldschmidt** and associates at the University of Oslo applied X-ray scattering to many common minerals determine the structures of crystals and formulated a set of rules for how elements are grouped

GOLDSCHMIDT®
Hawai'i 2022



Victor Moritz Goldschmidt

- *Norwegian mineralogist*
- *father of modern geochemistry*



GEOCHEMISCHE
VERTEILUNGSGESETZE
DER ELEMENTE

IX
DIE MENGENVERHÄLTNISSE DER ELEMENTE
UND DER ATOM-ARTEN

VON
V. M. GOLDSCHMIDT

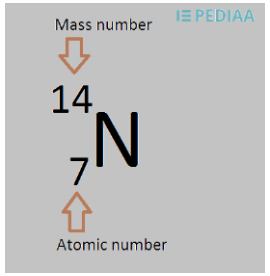
MIT 6 TEXTFIGUREN.

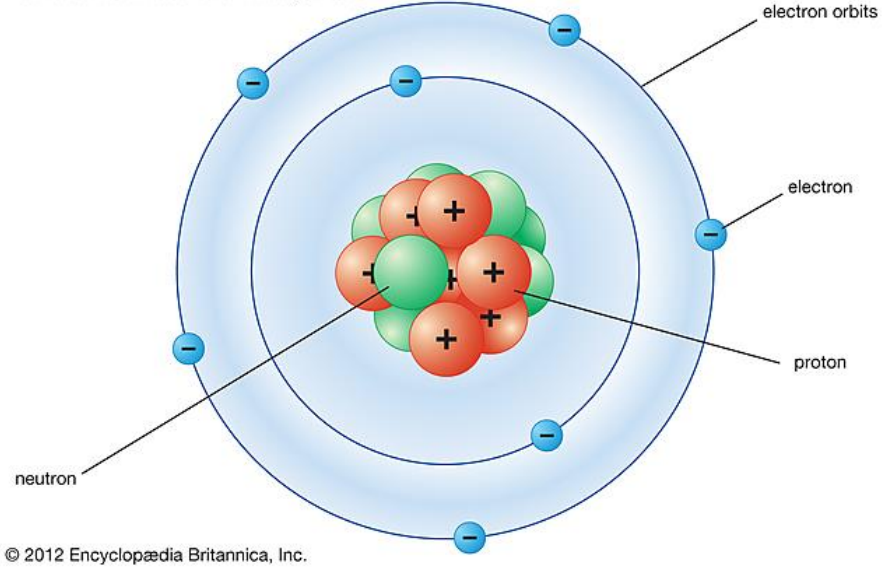
SKRIFTER UTGITT AV DET NORSKE VIDENSKAPS-AKADEMI I OSLO
I. MAT.-NATURV. KLASSE. 1937. No. 4

UTGITT FOR FRIDTJOF NANSENS FOND

OSLO
I KOMMISJON HOS JACOB DYBWAD
1938

Chemical elements - building blocks of materials





Bohr atomic model of a nitrogen atom

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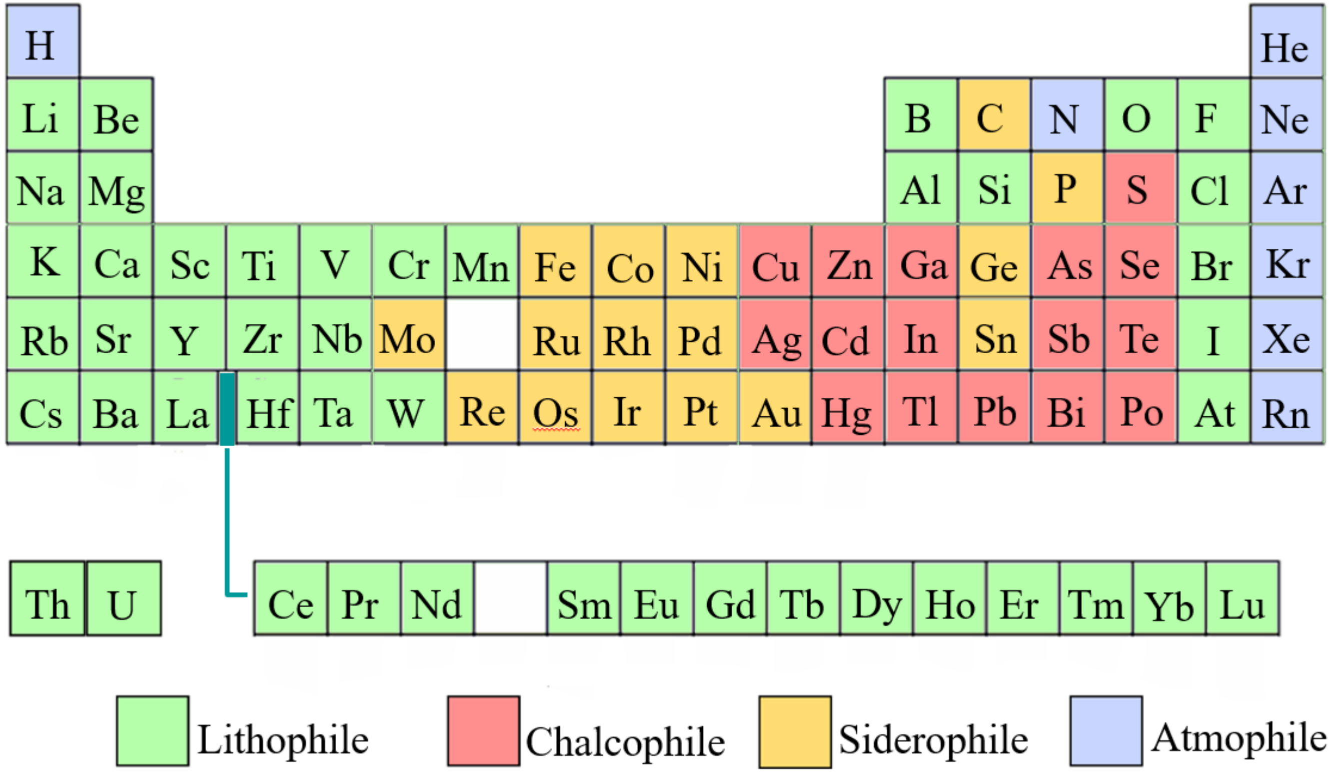
- identified by their atomic number Z (number of protons in the nucleus)
- an element can have more than one value for N (number of neutrons in the nucleus)
- the sum of these is the mass number (A), which is roughly equal to the atomic mass

- Atoms with the same atomic number but different neutron numbers are called isotopes
- 1700 known combinations of Z and N, of which only about 260 are refractory, remaining stable at high temperatures

The chemical behavior of an atom (affinity for other elements and the type of bonds it forms) is determined by the arrangement of electrons in orbitals, particularly the outermost (valence) electrons.



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Th	U	Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

🟩 Lithophile 🟥 Chalcophile 🟨 Siderophile 🟦 Atmophile

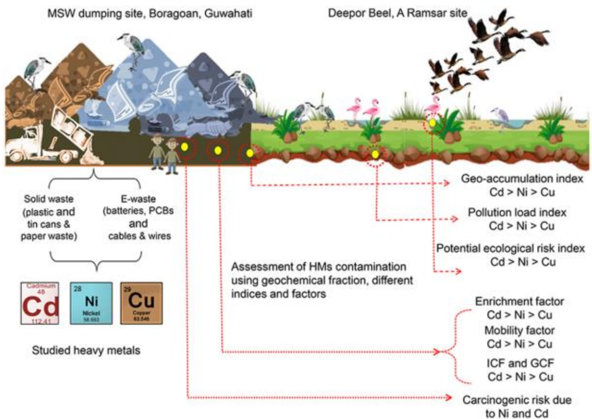
These arrangements are reflected in the position of elements in the periodic table

Lithophile el.combine easily with oxygen, they dominate in the Earth's crust rock and mantle (forming minerals)

Siderophile elements have an affinity for iron and tend to concentrate in the core

Chalcophile elements form sulphides

Atmophile elements dominate the atmosphere



Gujre, N., et al., 2021

locate contamination tracking anthropogenic pollutants

mineralogy — chemistry — intro geology

needed for

geochemistry

part of: climate change

part of: oceanography

key part of: **environmental geology**

key part of: **hydrogeology**

part of: atmospheric chemistry

key part of: **soil science**

key part of: **petrology**

key part of: **economic geology**

key part of: **biogeoscience**

includes: **geochemical modeling**

includes: **isotope geology**

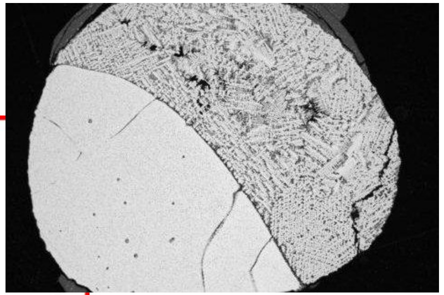
key part of: **organic geology**

key part of: **planetary geology**

key part of: **composition of Earth**

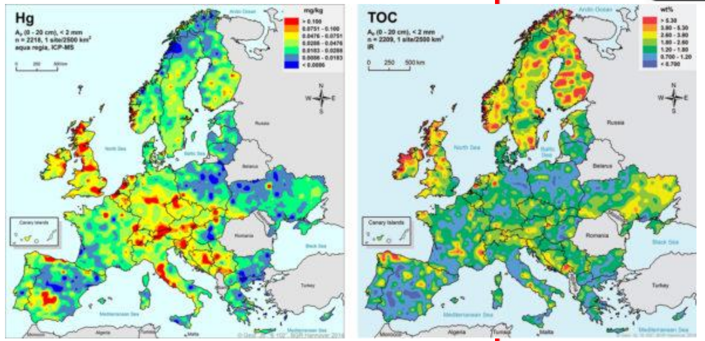
links to geochemistry

other important links



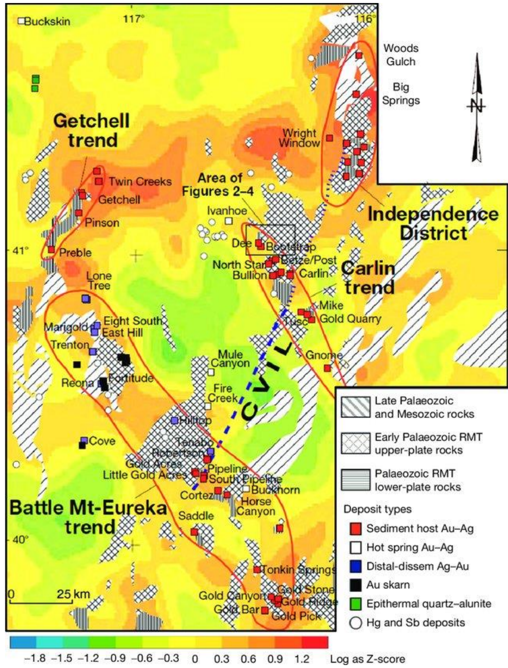
Ni, P. et al. 2020

iron isotopes → primordial bodies → initial chemical composition of their parent bodies



Reimann, C., et al., 2014

present the variation of selected elements on the surface



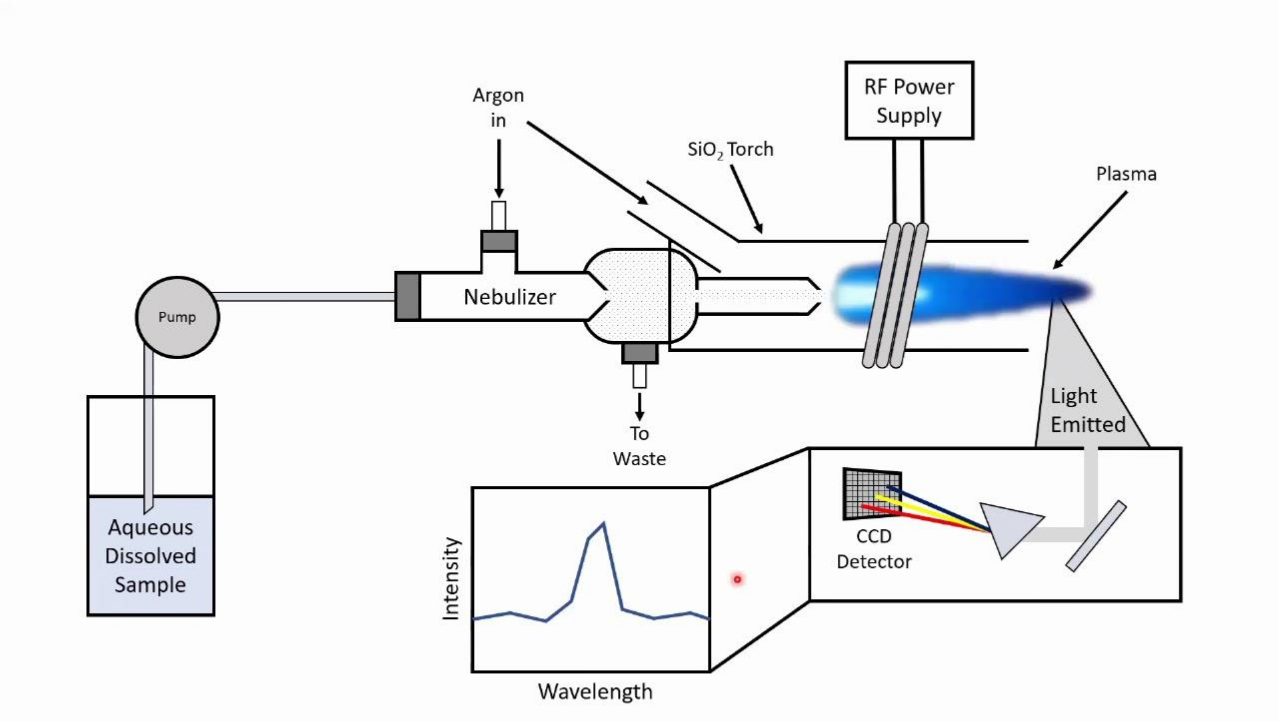
Cohen and Bowell, 2014

geochemical prospecting - ore exploration

What tools/methods do we use?

1. Major elements - XRF, ICP-OES and ICP-MS*
2. Trace elements - ICP-OES and ICP-MS
3. Isotope analyses - MC-ICPMS

*XRF - X-ray fluorescence;
ICP-OES - Inductively Coupled Plasma Optical Emission
ICP-MS - Mass Spectrometry
MC-ICPMS - Multicollector-Inductively Coupled Plasma Mass Spectrometer



Naele Z. et al., 2020

→ detailed chemical composition of geological samples

→ how a given geological system works

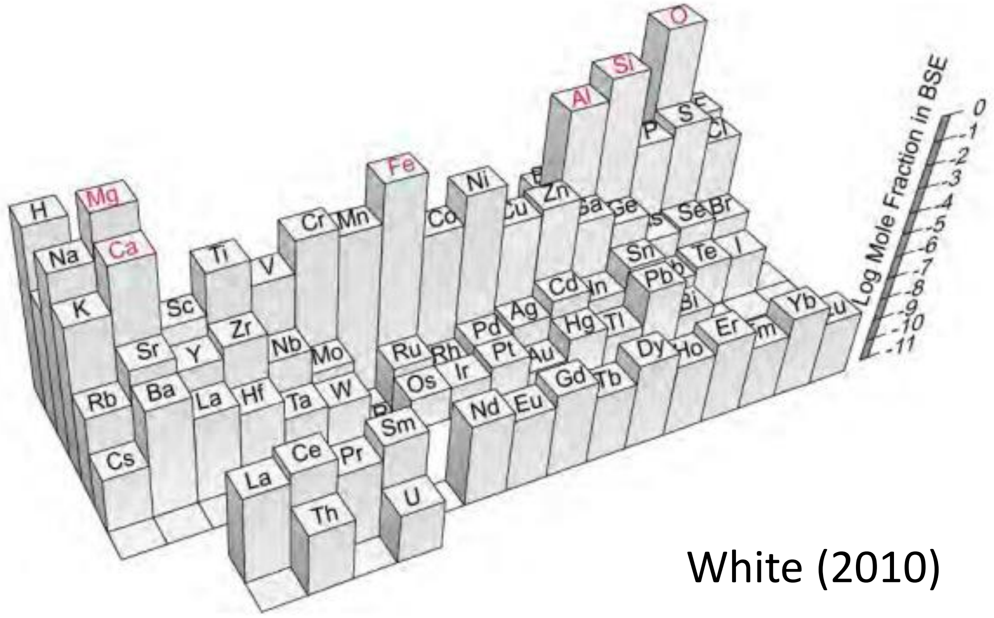
Major element analyses

Elements that form the bulk of analysed rock , variations in igneous rocks and minerals

99% of the Bulk Silicate Earth is comprised of around 7 elements

- Solar system: H, He
- Silicate Earth: O, Si, Al, Fe, Ca, Na, K, Mg
- Atmosphere: N, O, Ar
- Seawater: H, O, Na, Cl
- Core: Fe, Ni, Si?, K?

DEFINE
PHYSICAL
PROPERTIES
OF OBSERVED
MATERIAL!



White (2010)

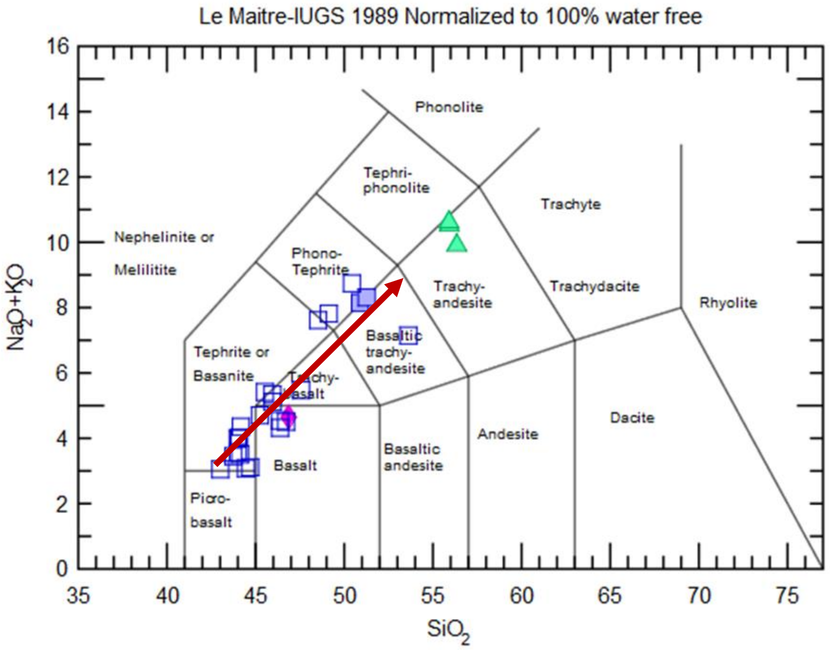
Granite vs. Basalt:

Granite: 70% SiO_2; 15% Al_2O_3; 6% Na_2O; 3% K_2O; >1% CaO, FeO, TiO_2 and MgO

Basalt: 45% SiO_2, 15% MgO; 13% Al_2O_3;10% FeO and CaO; >3% Na_2O, K_2O and TiO_2

Presenting the results

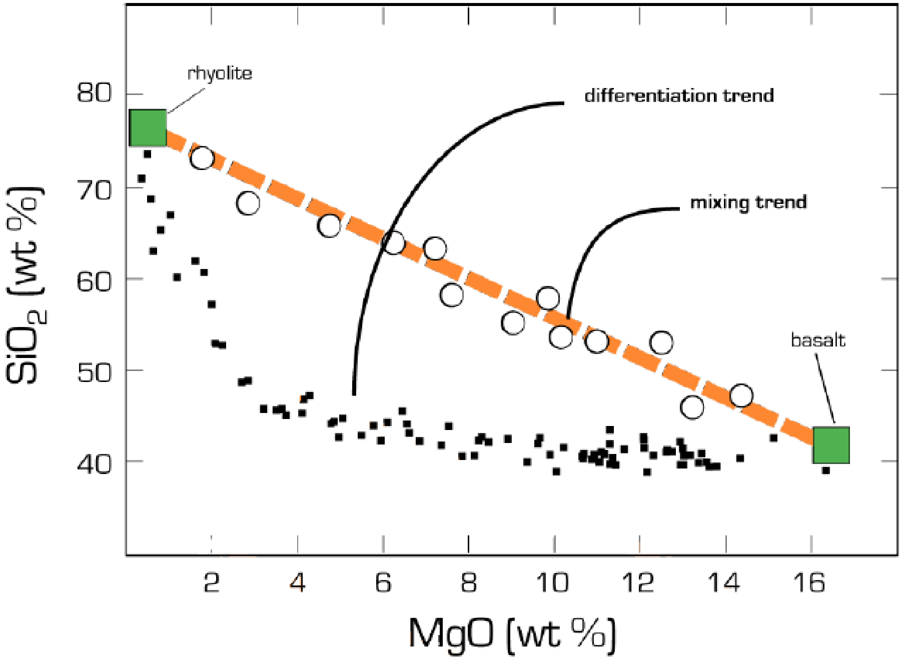
- Classifying igneous rocks – TAS diagram



Beloša et al. (in preparation)

TAS = Total Alkalis (Na2O + K2O) v SiO2
→ simple, easy to use and is applicable to a wide range of rock types, both glassy and non-glassy, volcanic and intrusive

- Using major elements to identify mixing between geological reservoirs – variation diagrams

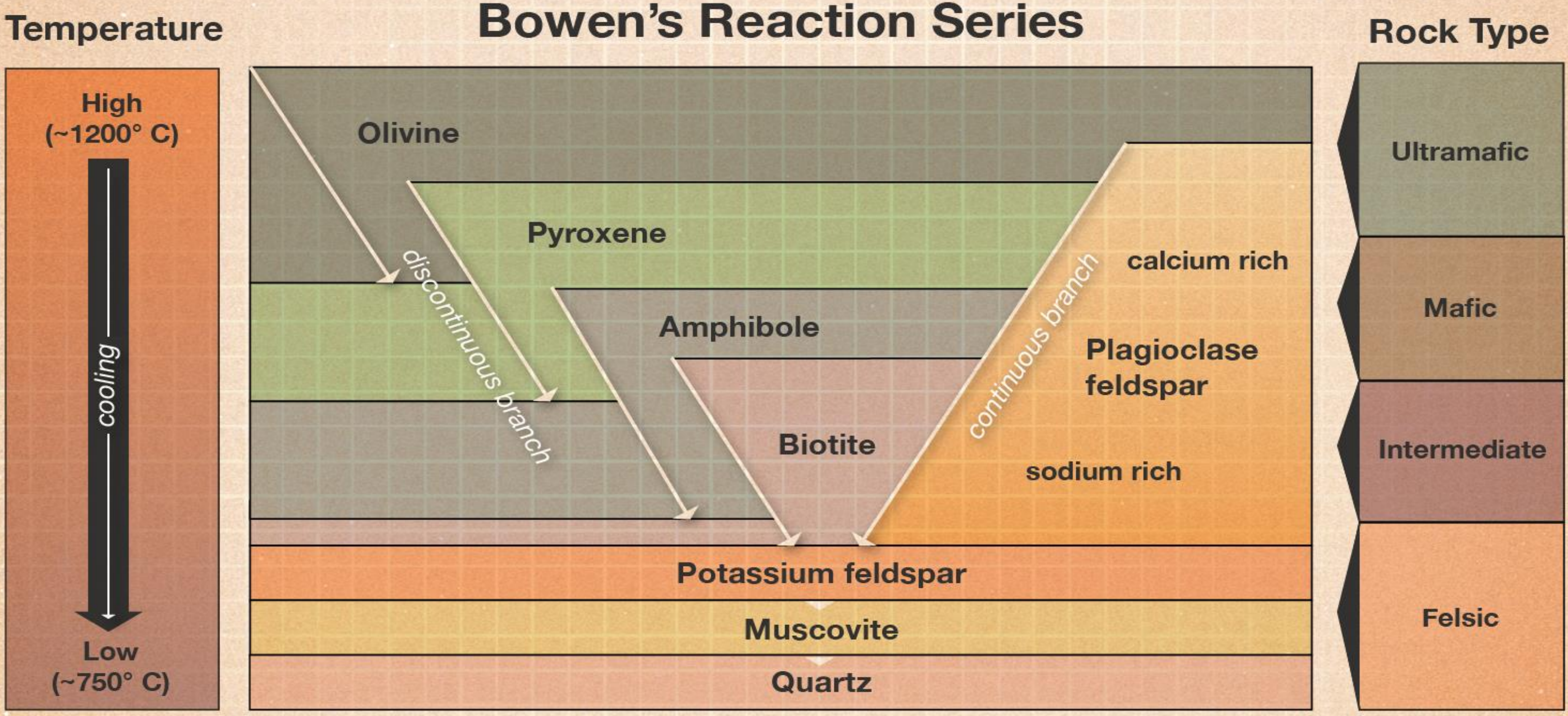


Millet et al. (2008)

Jet Propulsion Laboratory
California Institute of Technology

Magma bulk composition governs the minerals that crystallize to form an igneous rock and their chemical composition.

Bowen's Reaction Series



Limitations

- Not many elements to play with: limited range in chemical properties and applications

- Variations occuring during geological processes are rarely big

- Basalt: 45 wt% SiO2
- Andesite: 55 wt% SiO2

- Analytical errors are usually quite large compared to natural variations

Major elements provide useful constraints but usually do not allow investigation/quantification of geological processes with the required precision

Trace elements

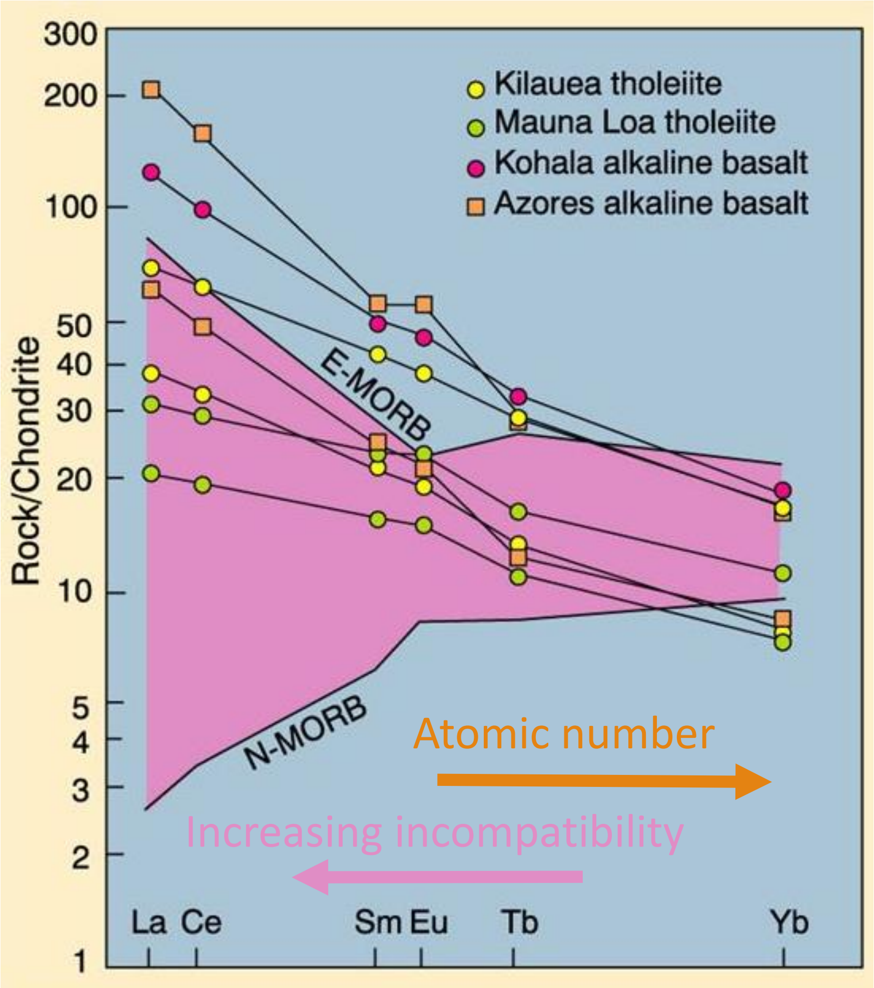
- ❑ NOT essential structural constituents of igneous minerals (measured in ppm or ppb not weight %)

- their concentration in a mineral governed by...

1. chemical equilibrium between phases (including melt)
2. ease with which a trace element substitutes into major element sites (i.e., function of ionic radii and charge - Goldschmidt's rules - model to explain trace element behavior, confirmed using thermodynamics and lattice strain models)

WHY USING TRACE ELEMENTS?

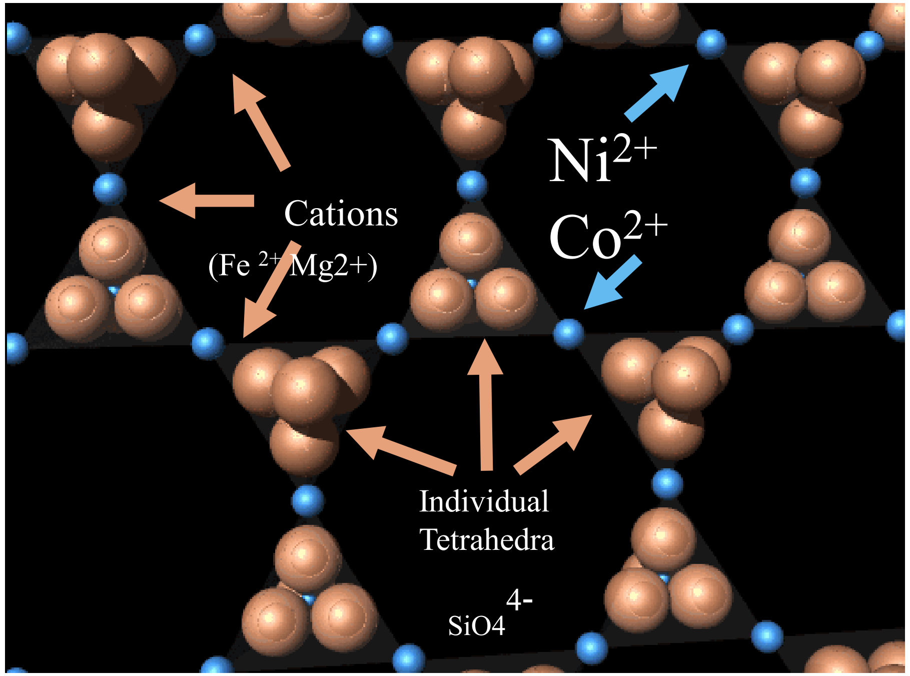
- major elements are insensitive to many processes – i.e., different flavours of basalt
- trace elements are sensitive to magma events (i.e. partial melting, fractional crystallisation)
- basis of nearly all radiogenic isotope systems
- lots of them (ca. 80)
- they show orders of magnitude variation in igneous rocks – from ppm to ppb



REE diagram for a typical E-MORB, N-MORB and OIB examples

After Wilson (1989)Igneous Petrogenesis

Fractionation of basalt by olivine crystallisation



Because of their similar ionic radius and charge, Ni2+ and Co2+ can
readily substitute for Fe2+ and Mg2+ in the olivine structure

*Compatible versus incompatible elements

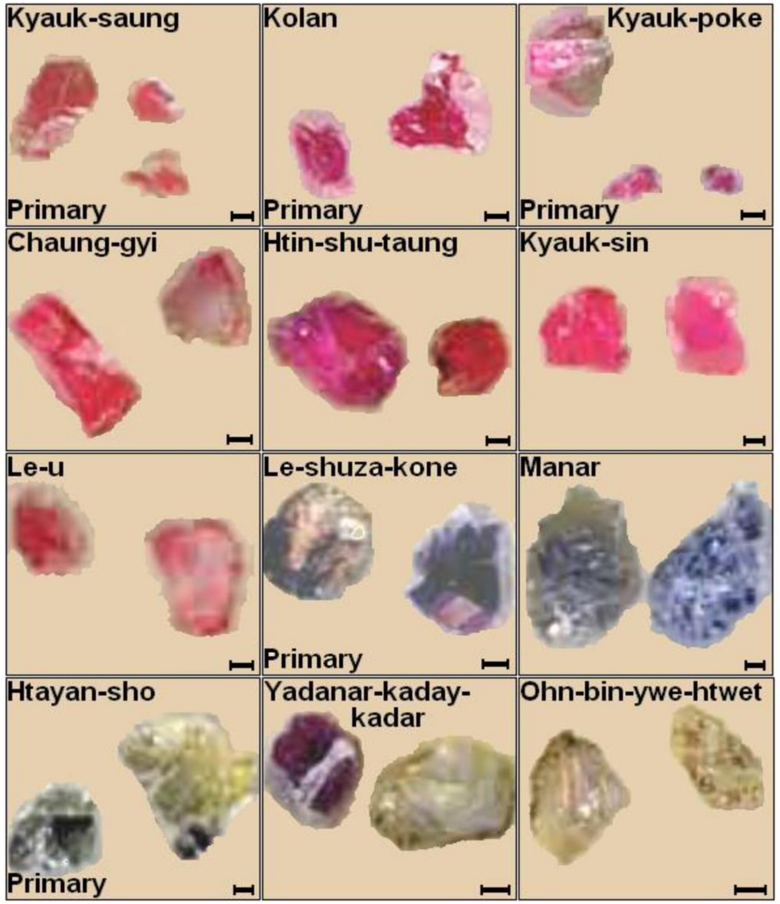
- Compatible trace elements favour crystals - olivine crystallisation

→ Ni will partition into olivine, depleting the residual melt in Ni–Kd = >1, in this case ~5

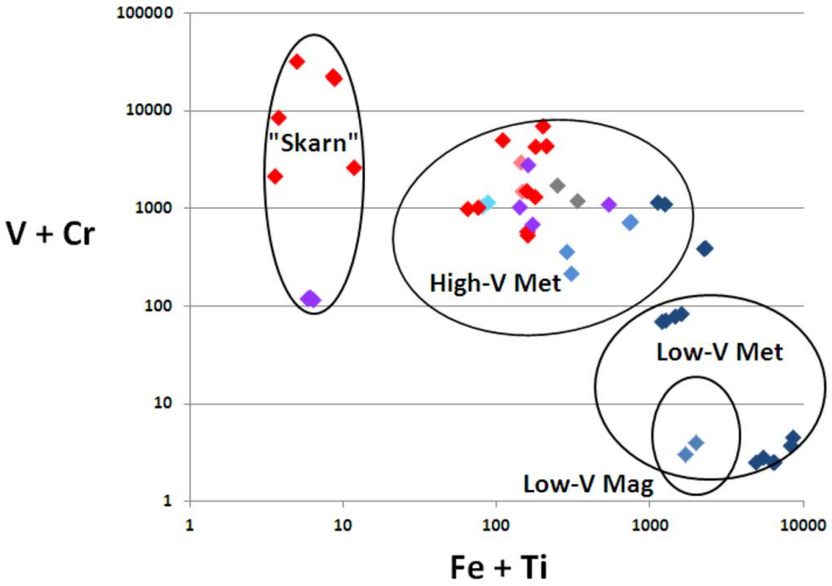
→ An incompatible element, such as Rb, will not enter olivine, but will concentrate in the evolving melt – in this case the Kd of Rb in olivine is << 1, in this case ~ 0.0001

Trace elements - example

- trace element signatures (LA-ICP-MS method)
- oxygen isotope values (δ18O, by laser fluorination)



Sutherland, F. et al., 2015



Sutherland, F. et al., 2015

→ expanded geochemical platform, provide a wider base for geographic corundum suites – identification for jewellery bussines

Isotopes

- Because different processes favor some isotopes over others, isotope ratios can be used to better understand e.g. how meteorites came to possess specific geochemical signatures

Used in 3 different ways:

- Radiogenic: isotopes created during radioactive decay – dating of samples
- Cosmogenic: isotopes generated by exposure of material to cosmic radiation
- Stable: small mass differences between isotopes

→ create isotopic variations during chemical reactions

→ trace chemical pathways and reactions

Notations

- Ratios measured are abundance ratios, not concentration (mass) ratios, can be presented as simple abundance ratios, or as deviations from a standard of reference

- This latter isotope is (almost) always a non radiogenic/cosmogenic isotope

e.g: 206Pb/204Pb, 208Pb/204Pb, 87Sr/86Sr, 56Fe/54Fe, 25Mg/24Mg

- For stable isotopes, deviations can be expressed as δ or ε

$$\delta = \frac{R_{sample} - R_{standard}}{R_{standard}} \text{ x } 1000 = \text{‰ difference}$$

$$\varepsilon = \frac{R_{sample} - R_{standard}}{R_{standard}} \text{ x } 10{,}000$$

Radiogenic isotopes: Tracers and Clocks

- Use the natural radioactive disintegration of unstable isotopes

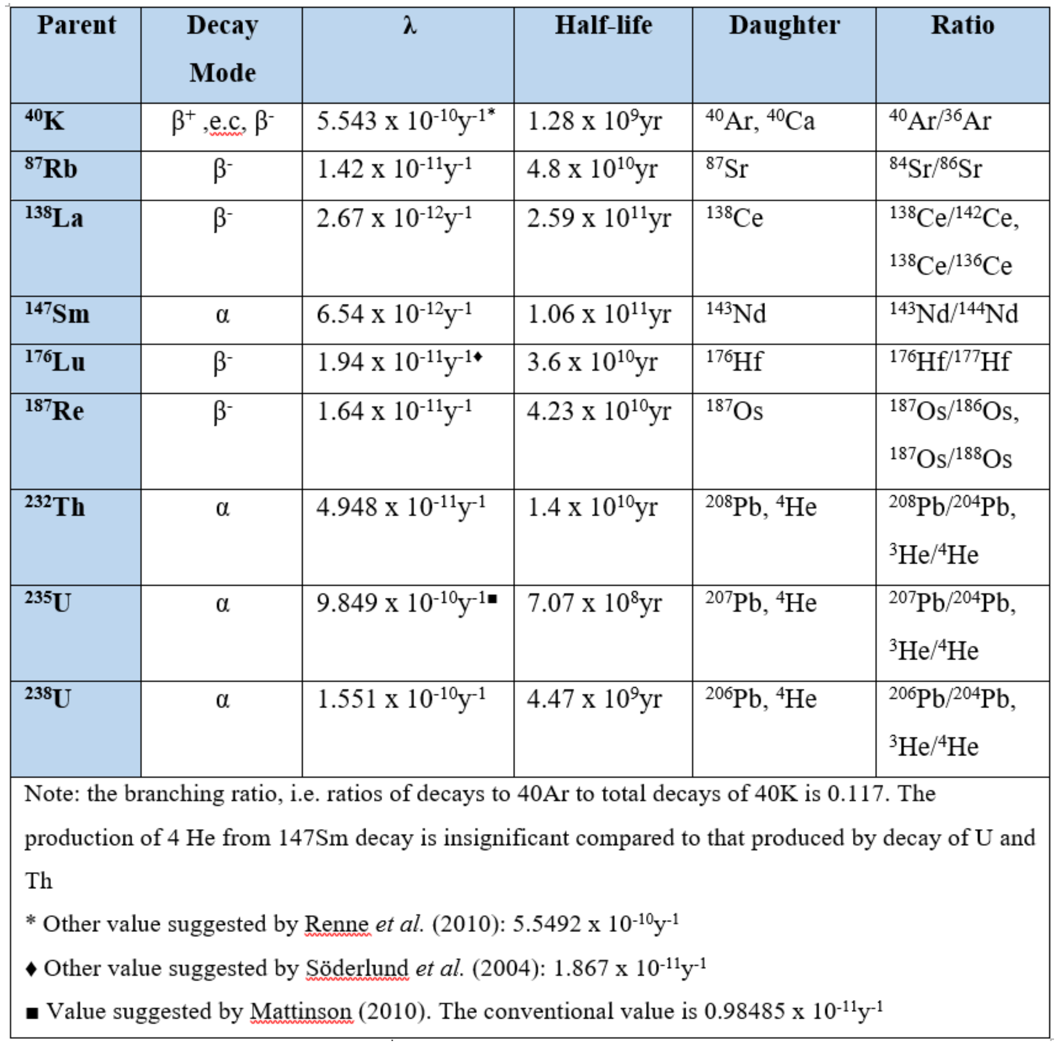
- 2 types of decay:

ß: $^{87}Rb \rightarrow {}^{87}Sr + e^- + v_e^-$
α: $^{147}Sm \rightarrow {}^{143}Nd + {}^{4}He$

→ Allow dating of rocks and minerals

→ The Rb-Sr system
→ **The Sm-Nd system**
→ The Lu-Hf system
→ The Re-Os system
→ The U-Th-Pb system

*Also, radiogenic isotope ratios are not fractionated during geological processes: perfect source tracers!



Parent	Decay Mode	λ	Half-life	Daughter	Ratio
^{40}K	β^+ ,e.c, β^-	$5.543 \times 10^{-10}y^{-1*}$	1.28×10^9yr	^{40}Ar, ^{40}Ca	$^{40}Ar/^{36}Ar$
^{87}Rb	β^-	$1.42 \times 10^{-11}y^{-1}$	4.8×10^{10}yr	^{87}Sr	$^{84}Sr/^{86}Sr$
^{138}La	β^-	$2.67 \times 10^{-12}y^{-1}$	2.59×10^{11}yr	^{138}Ce	$^{138}Ce/^{142}Ce$, $^{138}Ce/^{136}Ce$
^{147}Sm	α	$6.54 \times 10^{-12}y^{-1}$	1.06×10^{11}yr	^{143}Nd	$^{143}Nd/^{144}Nd$
^{176}Lu	β^-	$1.94 \times 10^{-11}y^{-1\blacklozenge}$	3.6×10^{10}yr	^{176}Hf	$^{176}Hf/^{177}Hf$
^{187}Re	β^-	$1.64 \times 10^{-11}y^{-1}$	4.23×10^{10}yr	^{187}Os	$^{187}Os/^{186}Os$, $^{187}Os/^{188}Os$
^{232}Th	α	$4.948 \times 10^{-11}y^{-1}$	1.4×10^{10}yr	^{208}Pb, ^{4}He	$^{208}Pb/^{204}Pb$, $^{3}He/^{4}He$
^{235}U	α	$9.849 \times 10^{-10}y^{-1\blacksquare}$	7.07×10^8yr	^{207}Pb, ^{4}He	$^{207}Pb/^{204}Pb$, $^{3}He/^{4}He$
^{238}U	α	$1.551 \times 10^{-10}y^{-1}$	4.47×10^9yr	^{206}Pb, ^{4}He	$^{206}Pb/^{204}Pb$, $^{3}He/^{4}He$

Note: the branching ratio, i.e. ratios of decays to 40Ar to total decays of 40K is 0.117. The production of 4 He from 147Sm decay is insignificant compared to that produced by decay of U and Th

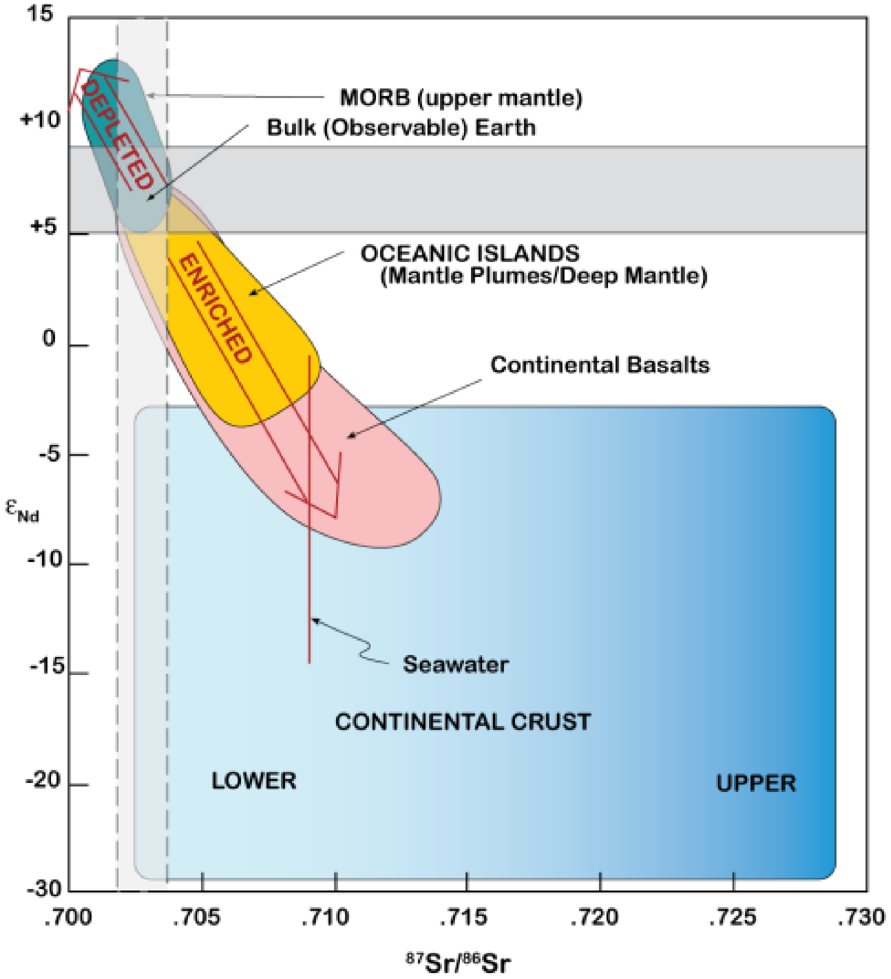
* Other value suggested by Renne *et al.* (2010): $5.5492 \times 10^{-10}y^{-1}$

♦ Other value suggested by Söderlund *et al.* (2004): $1.867 \times 10^{-11}y^{-1}$

■ Value suggested by Mattinson (2010). The conventional value is $0.98485 \times 10^{-11}y^{-1}$

Long-lived radioactive decay systems of geochemical interest, from White (2013)

“Mantle array”



Sr and Nd isotopic systematics of the crust and mantle, Earth’s major silicate reservoirs; White (2010)

In the case of Nd/Sm pair, both are refractory, both have similar properties → discuss the enrichment od depletion of reservoir

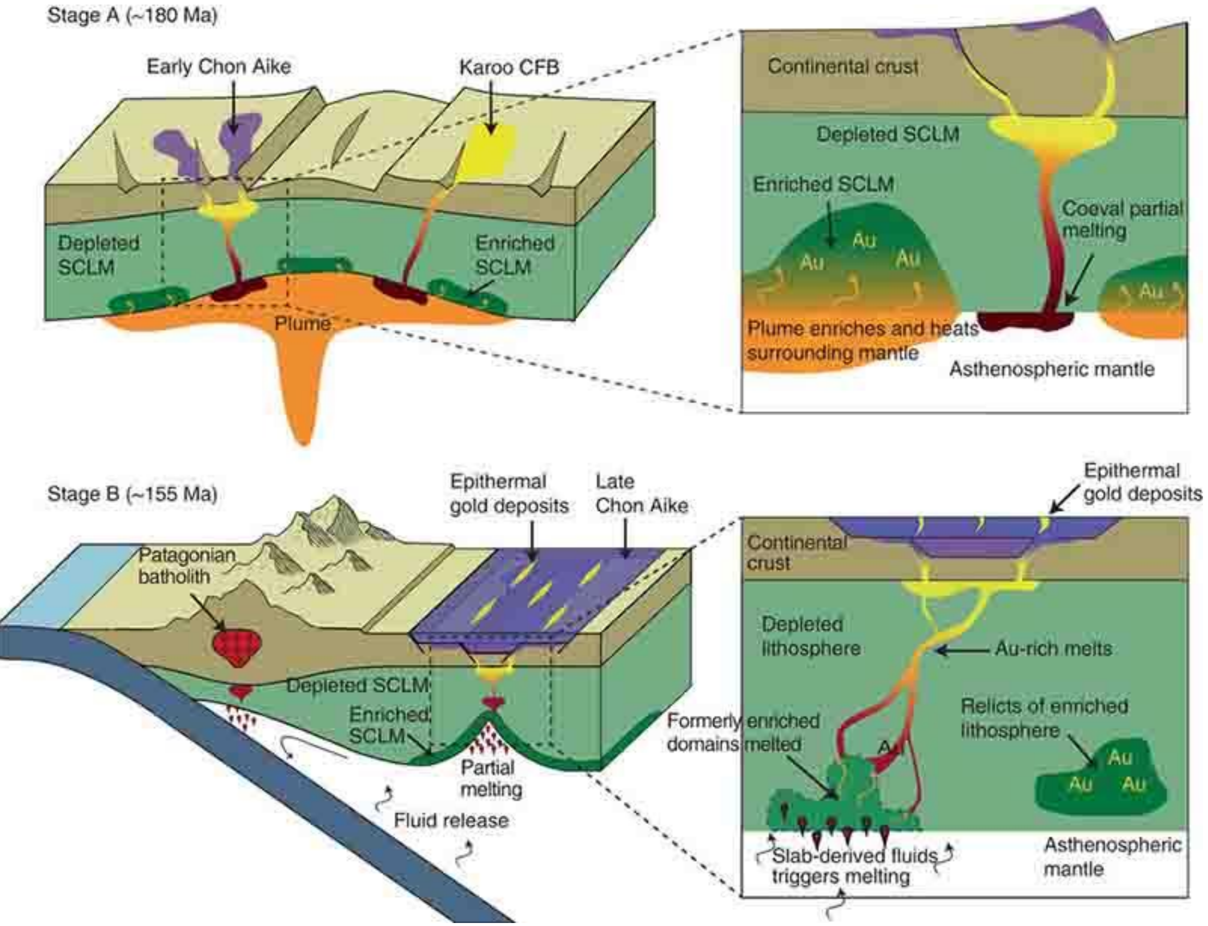
- Oceanic island basalts (OIB) and Mid-ocean ridge (MORB) basalts sample major reservoirs in the mantle
- Continental basalts represent mixtures of various components, including mantle plumes, subcontinental lithosphere, and continental crust

MORB: depleted in more incompatible elements, such as Rb and Nd compared to more compatible ones such as Sr and Sm

MORB also clearly have: more uniform isotopic compositions with less dispersion than OIB, implying the reservoir from which MORB are derived is less heterogeneous
→due to partial melting and extraction of the melt

Horizontal grey band is the estimated εNd of the bulk silicate of Caro and Bourdon (2010); vertical gray band between dashed lines in their estimated bulk silicate Earth 87Sr/86Sr

Geochemical definitions - *Griffin et al. (1999)* and *O'Reilly and Griffin (2010)*

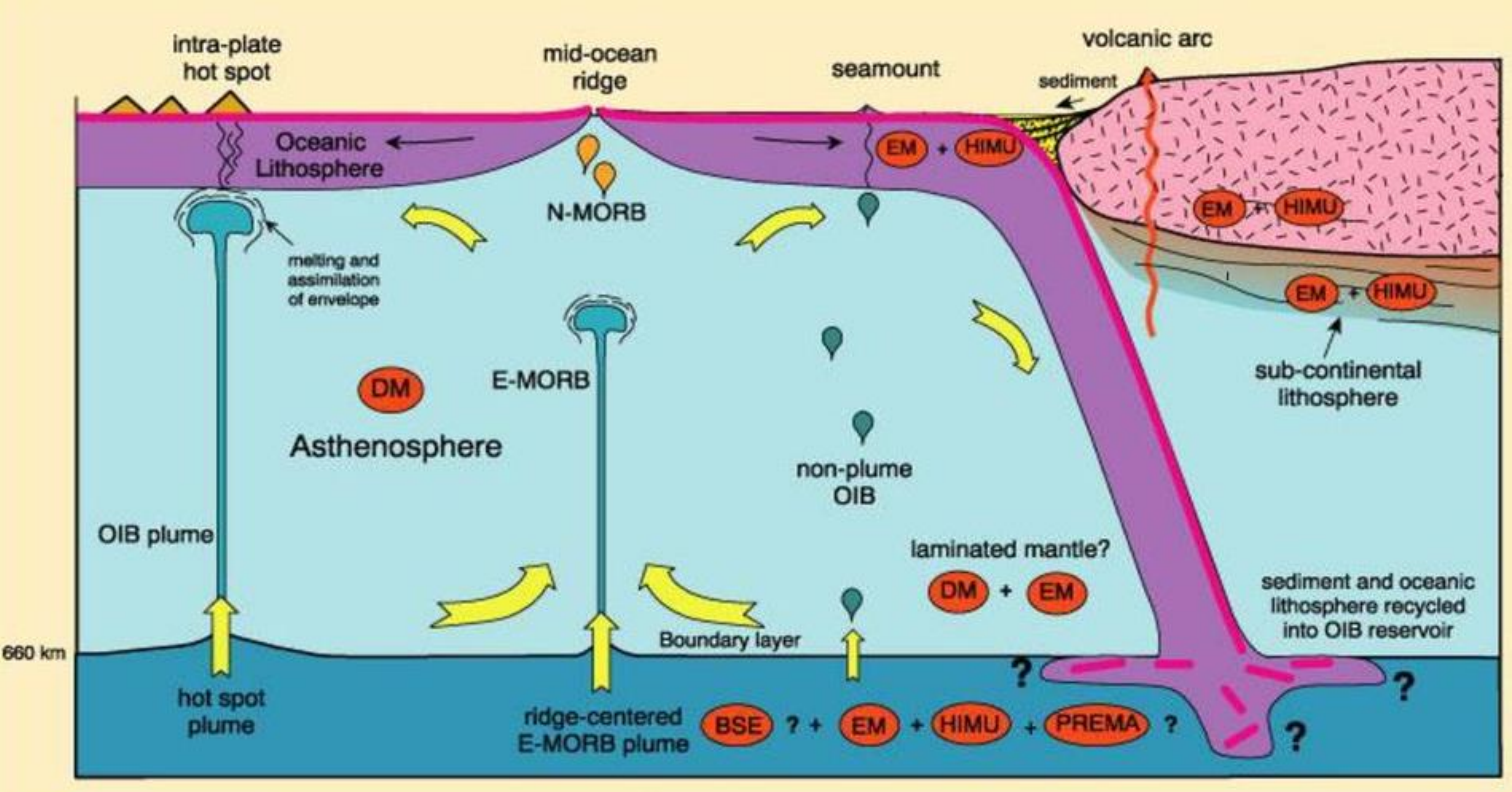


Plume-subduction interaction forms large auriferous provinces

Tassara, S. et al., 2017

- LITOSPHERE: Material that preserve distinct geochemical and isotopic signatures for longer periods than underlying convecting mantle
- UPPER MANTLE is that part of the mantle that provides uniform and depleted MORB and that formed by removal of the continental crust; it extends from the Moho to the 670km mantle discontinuity
- LOWER MANTLE is composed mostly of magnesium- and iron-bearing silicates, including the high-pressure equivalents of olivine and pyroxene

*SCLM – subcontinental lithospheric mantle



Winter (2001). Nomenclature from Zindler and Hart (1986). After Wilson (1989) and Rollinson (1993)

Mantle Reservoirs
(based on radiogenic isotopes)

BSE	Bulk Silicate Earth	Chondritic (undepleted) mantle
EMI	Enriched Mantle I	Low Sr^{87}/Sr^{86} mantle
EMII	Enriched Mantle II	Low Nd^{143}/Nd^{144} mantle
DM	Depleted Mantle	Previously melted mantle
HIMU	High μ Mantle	U-enriched mantle
PREMA	Prevalent Mantle	Chondritic (undepleted) mantle

From recycled ocean crust

What do we know about the lithosphere and astenosphere from geochemistry?

- Little is known about the transition zone or lower mantle

- More is known about the geochemistry of the upper mantle and lithosphere to depths of ~200 km because:

1. the mantle may be tectonically exposed at the Earth's surface in ultramafic massifs

2. ultramafic xenoliths, which are direct samples of the mantle, are transported to the Earth's surface in ascending magmas in both oceanic and continental regions

3. common mafic and rare ultramafic magmas (products of partial melting within the mantle) are at relatively shallow depths, and can exposed at the Earth's surface

4. conditions of temperature and pressure within the mantle are easily attained in experimental studies, thus allowing the testing of mantle models

5. mantle structure can be determined more precisely by geophysical studies

Differentiation and Fractionation

- The chemical composition of the Earth and other bodies is determined by these two opposing processes

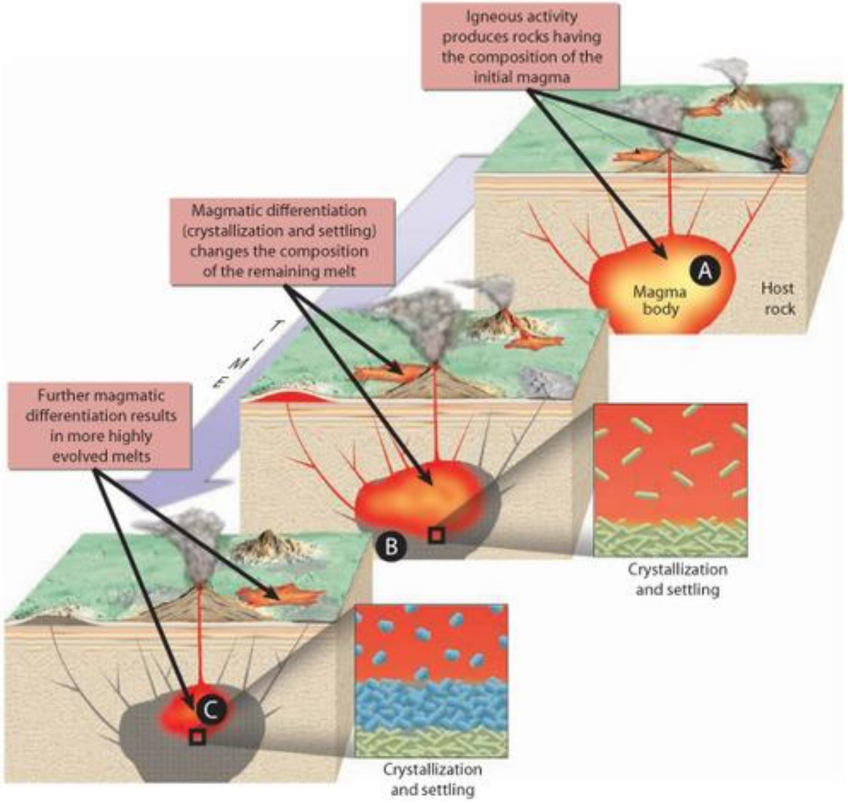
- differentiation occurs at mid-ocean ridges through partial melting , with more refractory materials remaining at the base of the lithosphere, while the remainder rises to form basalt

- a major source of differentiation is fractionation, an unequal distribution of elements and isotopes

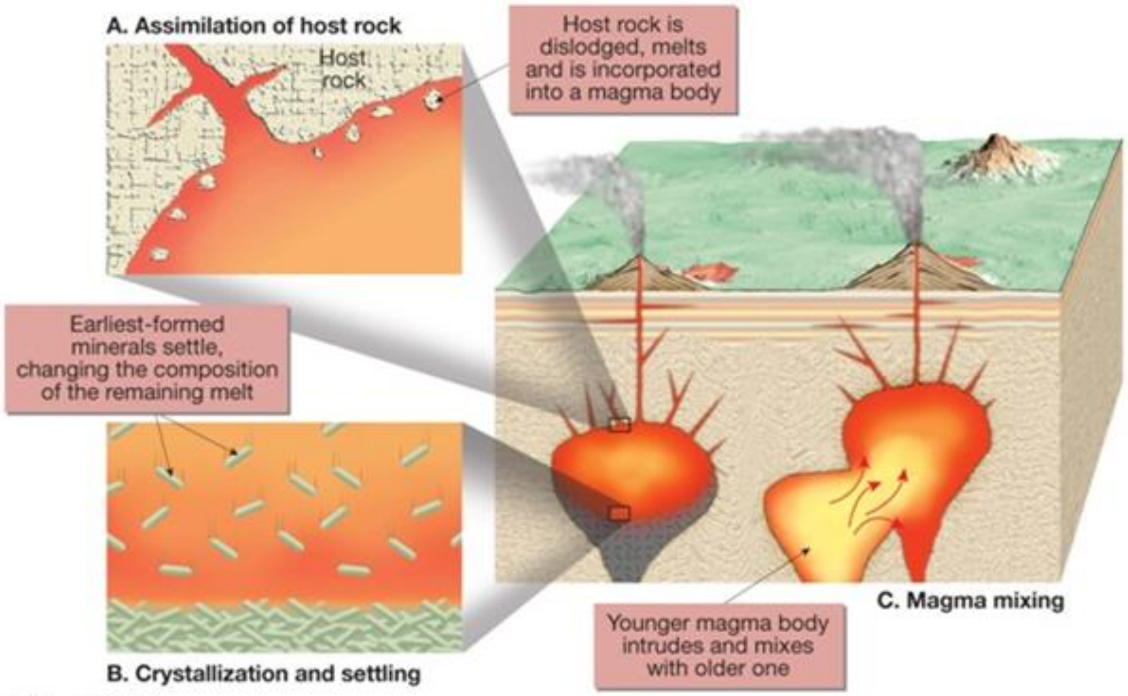
→ result of chemical reactions, phase changes, kinetic effects, or radioactivity

(i.e. the terrestrial planets formed iron-rich cores and silicate-rich mantles and crusts)

- in the Earth's mantle, the primary source of chemical differentiation is partial melting, particularly near mid-ocean ridges
- this can occur when the solid is heterogeneous or a solid solution, and part of the melt is separated from the solid
- The process is known as equilibrium or batch melting if the solid and melt remain in equilibrium until the moment that the melt is removed, and fractional or Rayleigh melting if it is removed continuously



Magma mixing



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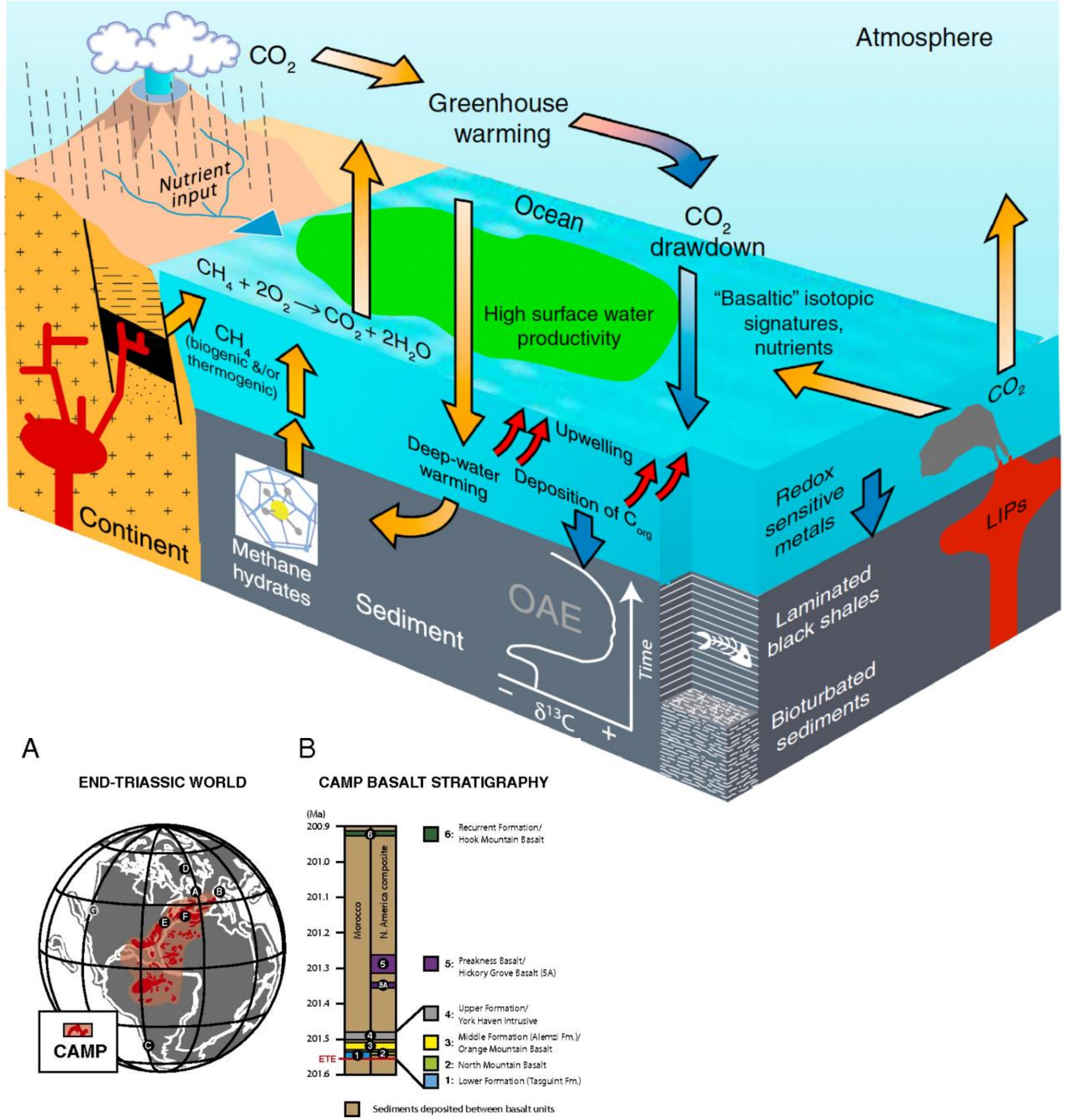
- after an oceanic plate descends into the mantle, convection eventually mixes the two parts together



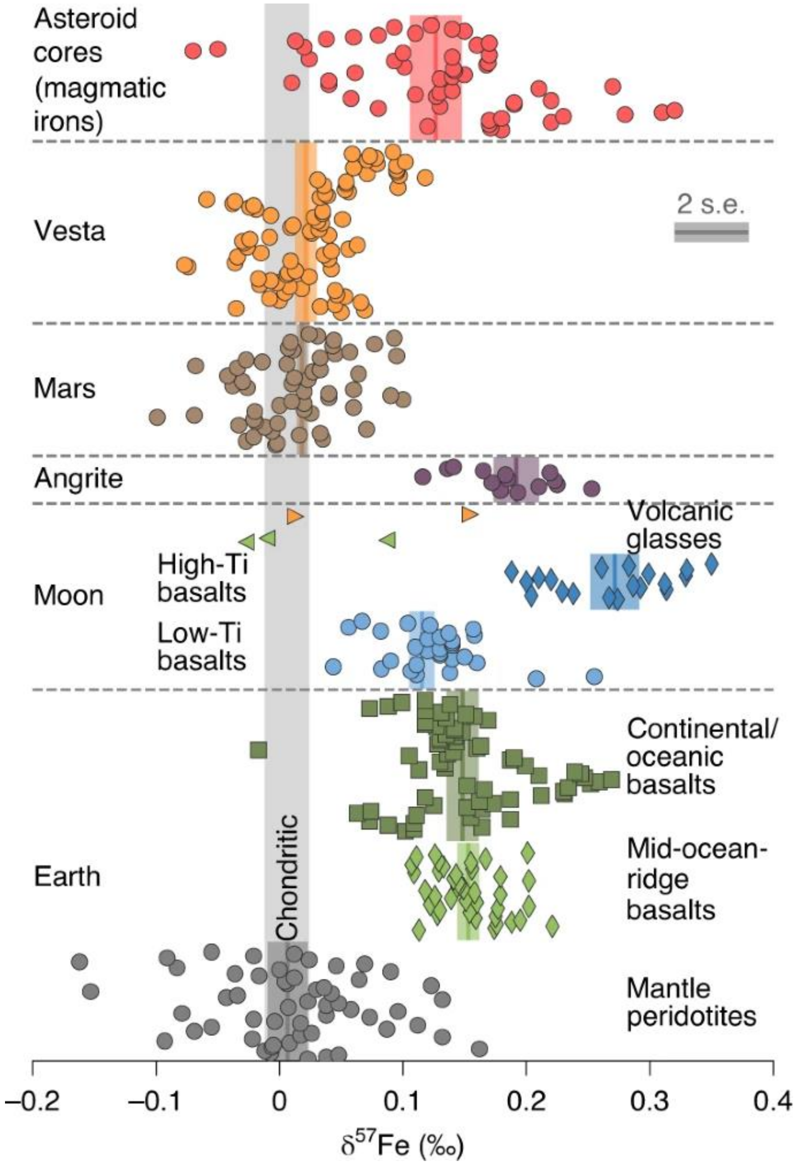
Percival, Lawrence ME, et al. (2017)

Carbon-isotopes can be used to trace major perturbations to the global carbon cycle (such as input of isotopically light methane/CO2, or the large-scale burial of organic matter)

Osmium isotopes can be used to track increases in volcanic activity and/or continental weathering rates

Mercury concentrations can be used as another proxy of volcanism

Therefore, by combining these proxies in sedimentary records of these two events, it is possible to show how multiple surface processes on Planet Earth were operating and interacting during times of major environmental perturbation.



Fe isotopic compositions for various types of terrestrial and extraterrestrial samples

Ni, P. et al. 2020

Iron meteorites record a history of planetary-scale processes such as accretion, melting and differentiation

As their cores cooled and solidified, substantial chemical fractionation occurred due to solid metal–liquid metal fractionation

Iron isotope analyses of iron meteorites found their $^{57}Fe/^{54}Fe$ ratios to be heavier than chondritic by approximately 0.1 to 0.2 per mil for most meteorites, indicating that a common parent body process was responsible

Here we experimentally show that the iron isotopic composition of iron meteorites can be explained solely by core crystallization

Supplimentary material