Mid-course checkpoint

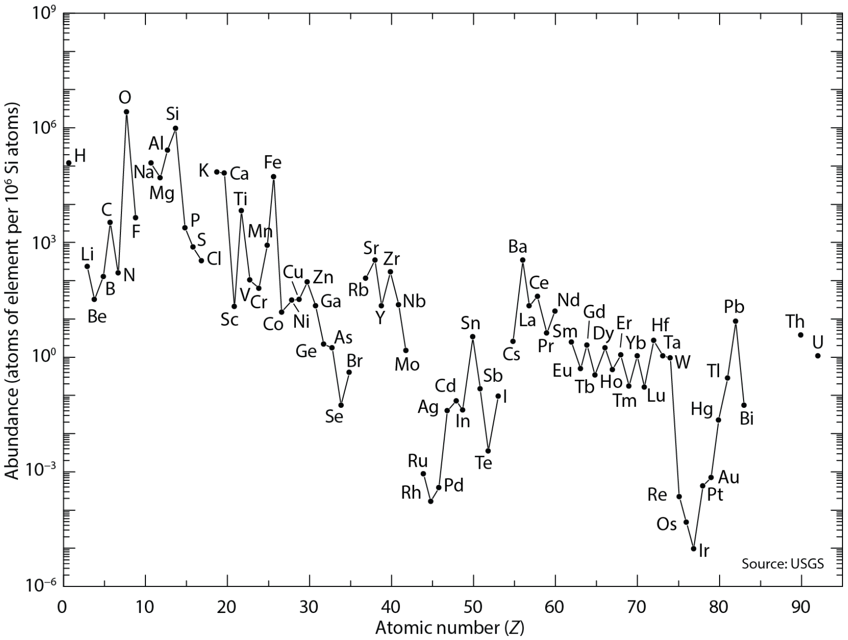
Week	Lect.	Date	Topic
Week 1	1	Mon 9.1.	Structure of crystalline materials. Symmetry.
Structure	2	Tue 10.1.	Structural databases, visualization of crystal structures.
Week 2	3	Mon 16.1.	Bonding in solids. Description of crystal structures.
Bonding	4	Tue 17.1.	Band theory. Band structures.
Week 3	5	Mon 23.1.	Phase diagrams, crystal growth.
Synthesis	6	Tue 24.1.	Solid state synthesis.
Week 4	7	Mon 30.1.	XRD, Miller indices. Powder XRD databases. Microscopies.
Characterization	8	Tue 31.1.	Spectroscopies and thermal analysis.
Week 5	9	Mon 6.2.	Abundance of elements, geochemistry, minerals.
Main groups	10	Tue 7.2.	Main group compounds, allotropes, Zintl phases.
Week 6	11	Mon 13.2.	*d*-block metals, ligand field theory, magnetism.
d-block metals	12	Tue 14.2.	*d*-block metal oxides and other compounds.
Examination week for study period III (no lectures).			
Week 7	13	Mon 27.2.	**12.15-14.00, C100**. Defects, non-stoichiometric compounds.
Defects and doping	14	**Fri** 3.3.	**10.15-12.00, C100**. Semiconductors, doping.
Final Wiki project deadline 20.3.			

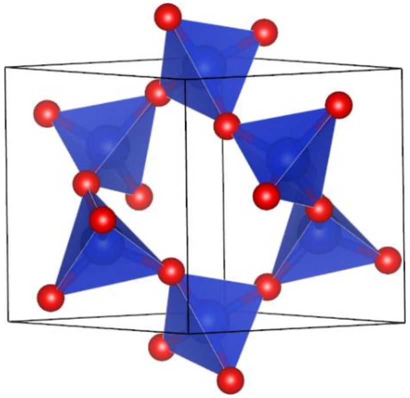
The first version of the Wiki project should be ready by 26.2.

Lecture 9: Geochemistry, minerals

- Geochemistry
  - The origin and abundance of elements
  - Goldchmidt classification
  - Accessibility and supply of elements

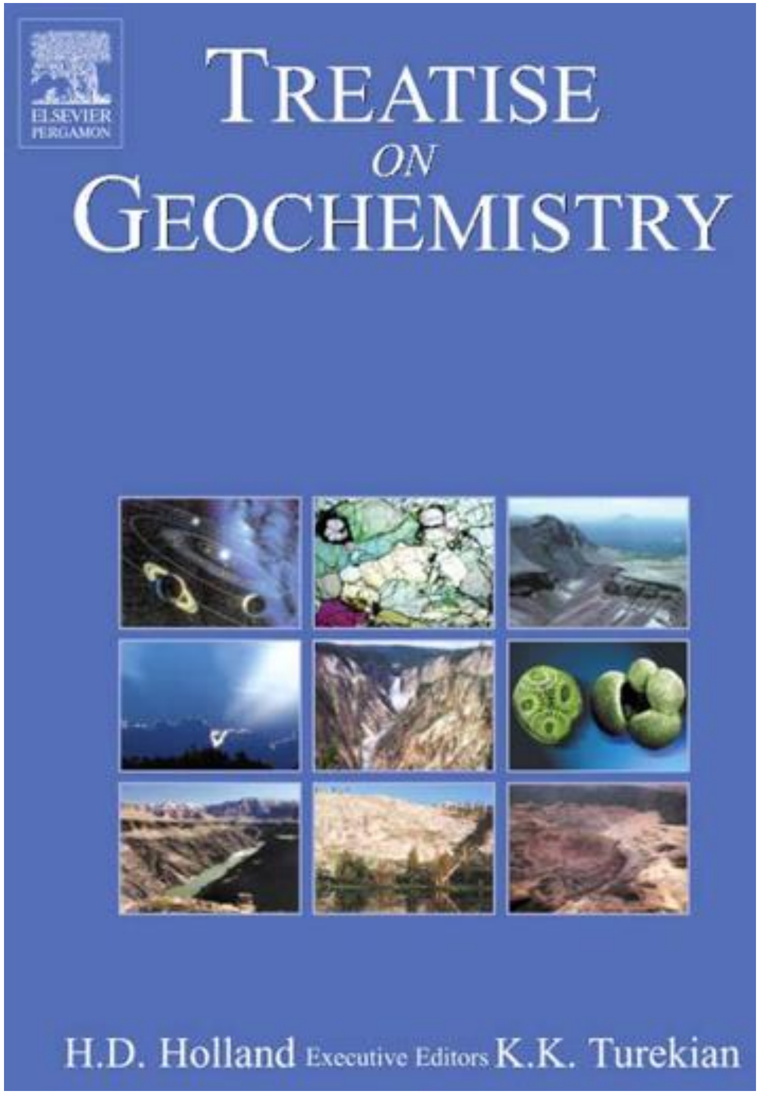
- Minerals
  - Systematic classification
  - Silicates
  - Aluminosilicates
  - Hardness as an example of a physical property





Figures: AJK

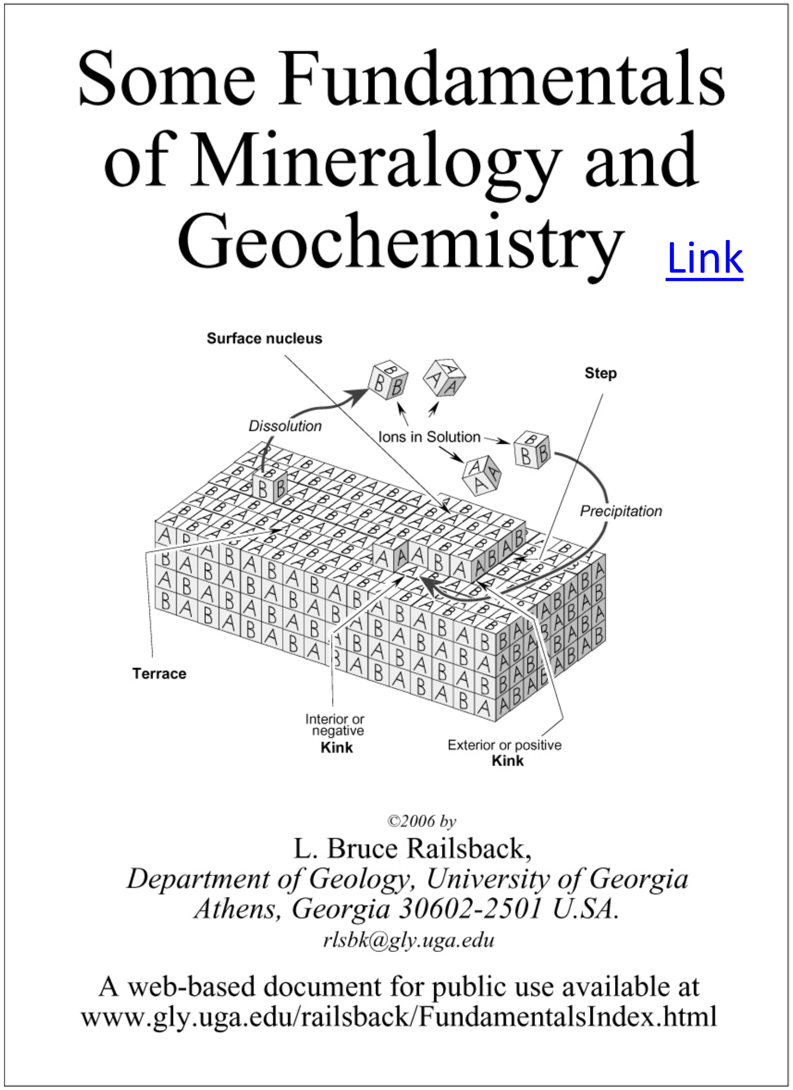
Literature



ELSEVIER PERGAMON

TREATISE ON GEOCHEMISTRY

H.D. Holland Executive Editors K.K. Turekian



Some Fundamentals of Mineralogy and Geochemistry Link

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A web-based document for public use available at www.gly.uga.edu/railsback/FundamentalsIndex.html

The origin of chemical elements

- Big Bang nucleosynthesis (H, He, some Li)
- Stellar nucleosynthesis
  - Elements up to Ni are created by fusion reactions (see Table below)
- Elements heavier than Ni are created by neutron and proton capture processes
  - Supernova nucleosynthesis and merging neutron stars (ongoing research!)

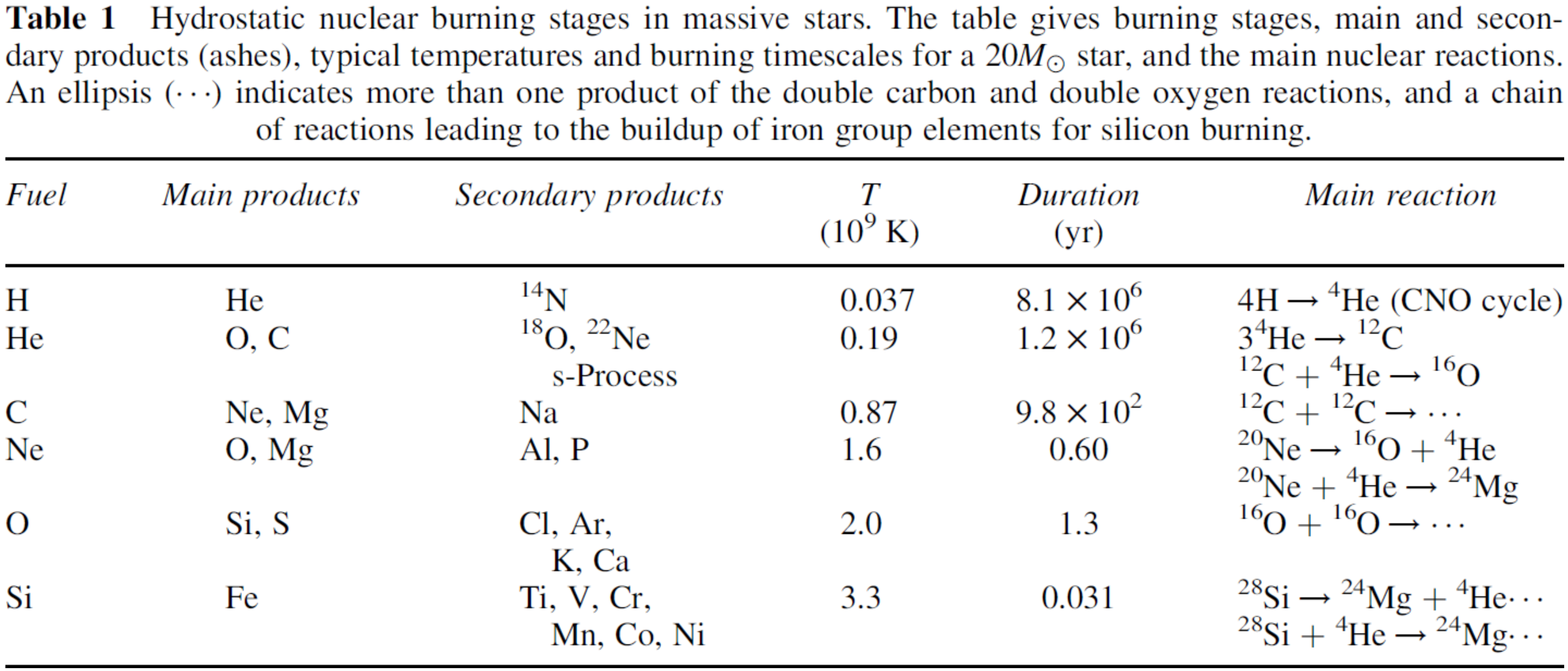
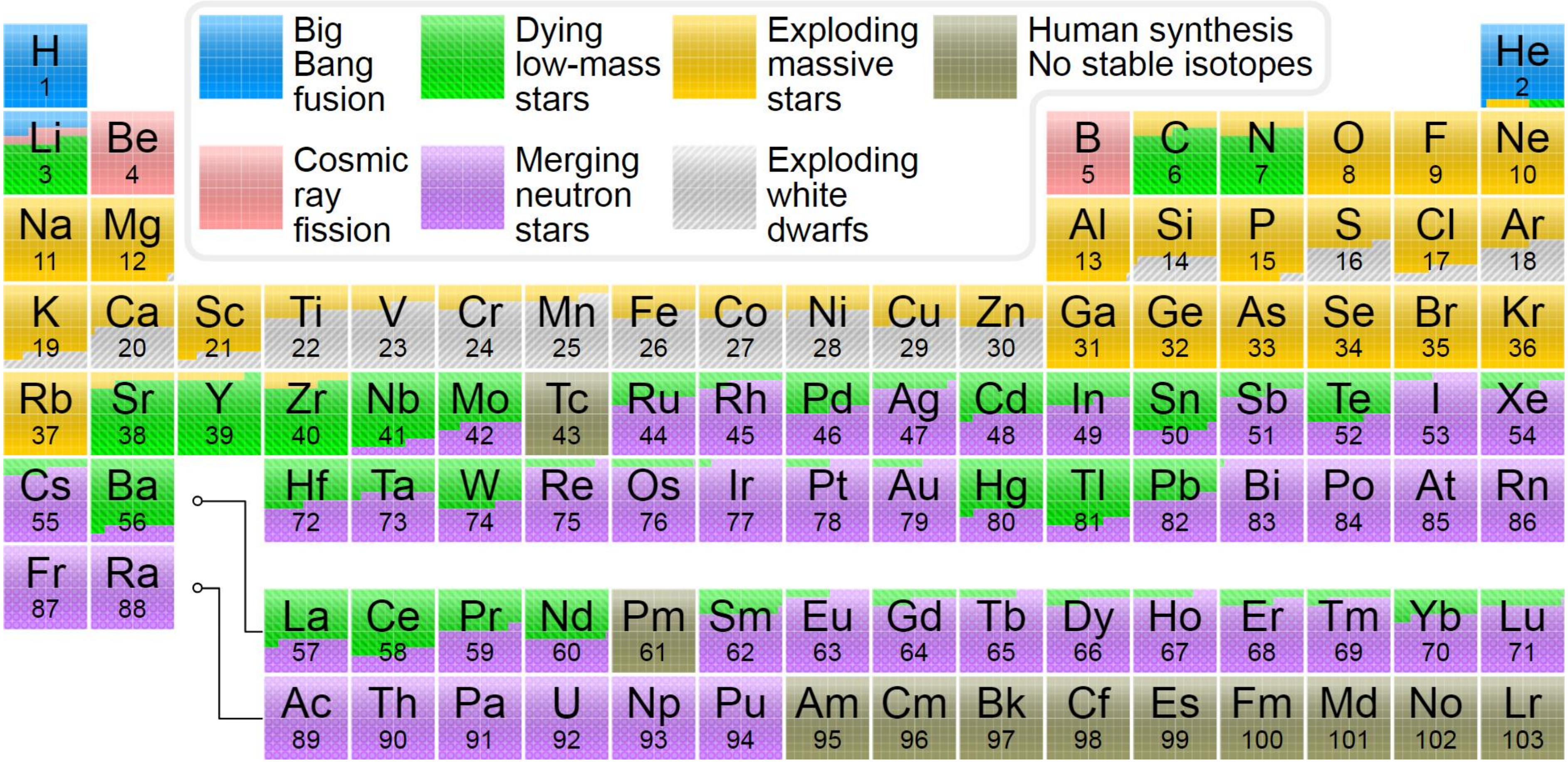


Table 1 Hydrostatic nuclear burning stages in massive stars. The table gives burning stages, main and secondary products (ashes), typical temperatures and burning timescales for a $20M_\odot$ star, and the main nuclear reactions. An ellipsis ($\cdots$) indicates more than one product of the double carbon and double oxygen reactions, and a chain of reactions leading to the buildup of iron group elements for silicon burning.

Fuel	*Main products*	*Secondary products*	*T* (10^9 K)	*Duration* (yr)	*Main reaction*
H	He	^{14}N	0.037	8.1×10^6	$4H \rightarrow {}^4He$ (CNO cycle)
He	O, C	^{18}O, ^{22}Ne s-Process	0.19	1.2×10^6	$3\,{}^4He \rightarrow {}^{12}C$ $^{12}C + {}^4He \rightarrow {}^{16}O$
C	Ne, Mg	Na	0.87	9.8×10^2	$^{12}C + {}^{12}C \rightarrow \cdots$
Ne	O, Mg	Al, P	1.6	0.60	$^{20}Ne \rightarrow {}^{16}O + {}^4He$ $^{20}Ne + {}^4He \rightarrow {}^{24}Mg$
O	Si, S	Cl, Ar, K, Ca	2.0	1.3	$^{16}O + {}^{16}O \rightarrow \cdots$
Si	Fe	Ti, V, Cr, Mn, Co, Ni	3.3	0.031	$^{28}Si \rightarrow {}^{24}Mg + {}^4He \cdots$ $^{28}Si + {}^4He \rightarrow {}^{24}Mg \cdots$

Ref: Treatise on Geochemistry, Vol 1, p. 9

Main origin of chemical elements



Big Bang fusion

Dying low-mass stars

Exploding massive stars

Human synthesis No stable isotopes

Cosmic ray fission

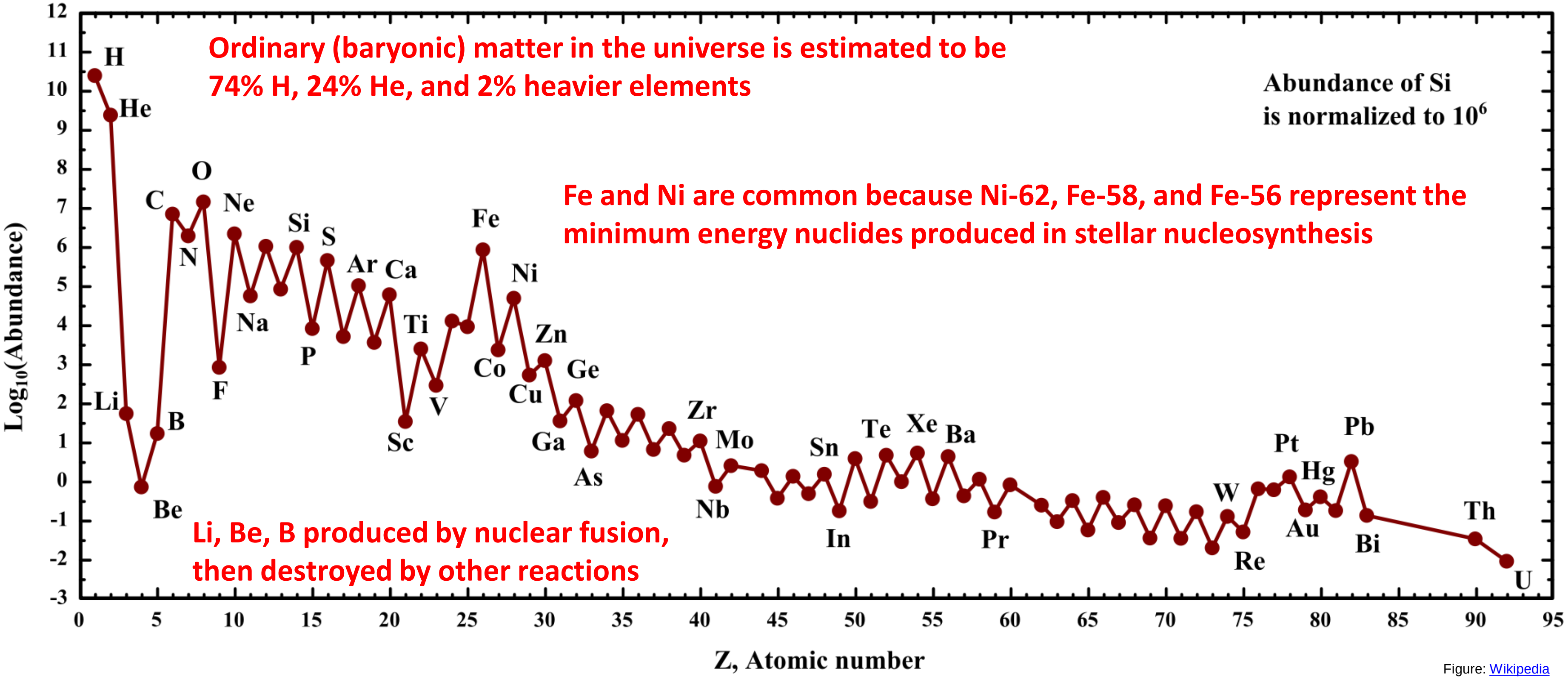
Merging neutron stars

Exploding white dwarfs

Figure: [Wikipedia]

https://en.wikipedia.org/wiki/Stellar_nucleosynthesis
https://en.wikipedia.org/wiki/Supernova_nucleosynthesis
http://blog.sdss.org/2017/01/09/origin-of-the-elements-in-the-solar-system/

Abundances of the elements in the Solar system



Ordinary (baryonic) matter in the universe is estimated to be 74% H, 24% He, and 2% heavier elements

Fe and Ni are common because Ni-62, Fe-58, and Fe-56 represent the minimum energy nuclides produced in stellar nucleosynthesis

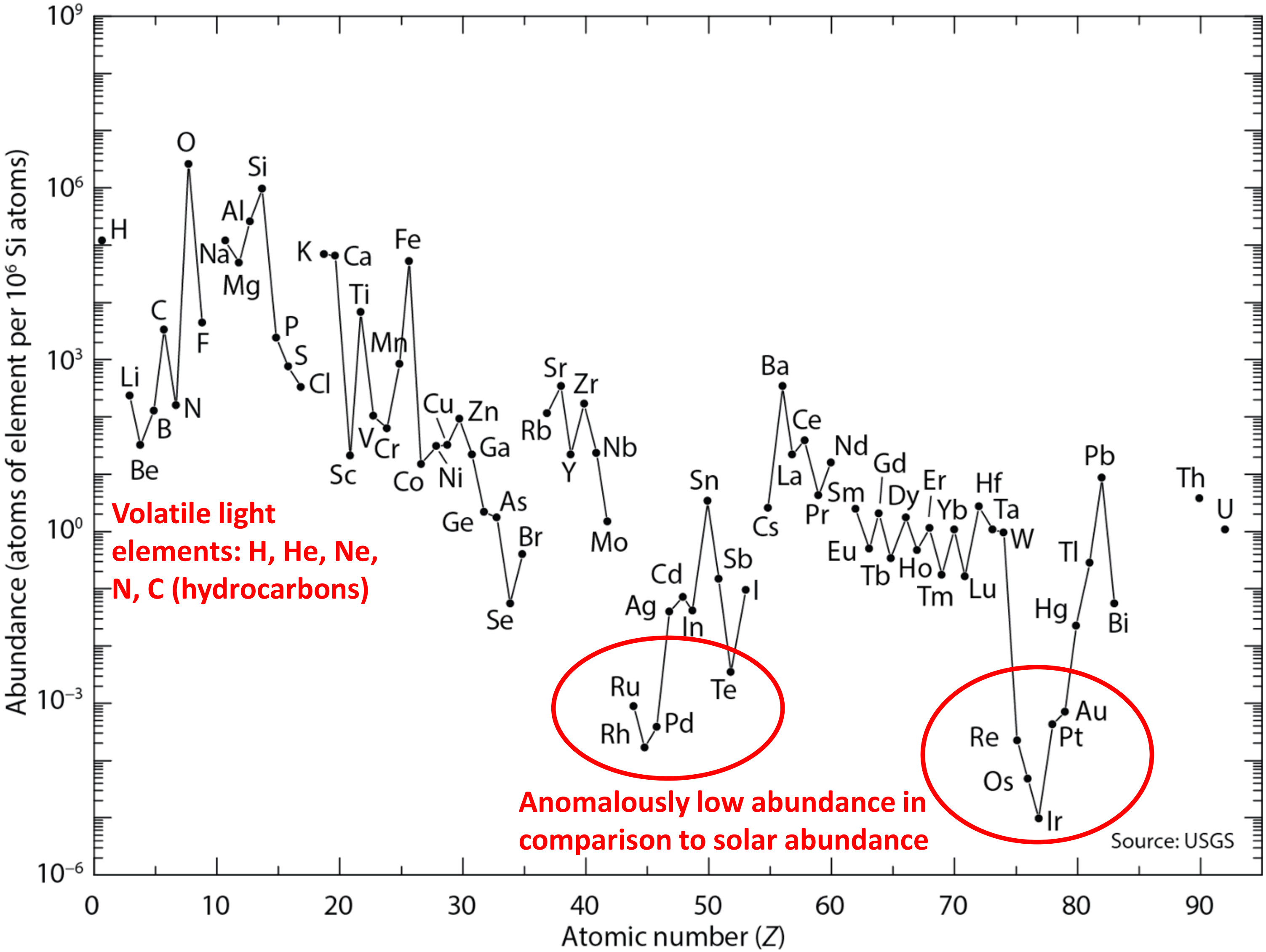
Li, Be, B produced by nuclear fusion, then destroyed by other reactions

Figure: Wikipedia

Two general trends:

1. A decrease in abundance as elements become heavier
2. An alternation of abundance in elements as they have even or odd atomic numbers (the Oddo-Harkins rule, arises from the details of the helium burning process)

Abundances of the elements in the Earth's crust



Volatile light elements: H, He, Ne, N, C (hydrocarbons)

Anomalously low abundance in comparison to solar abundance

Source: USGS

Figure: AJK

Abundance and form of the most abundant elements in Earth's continental crust.

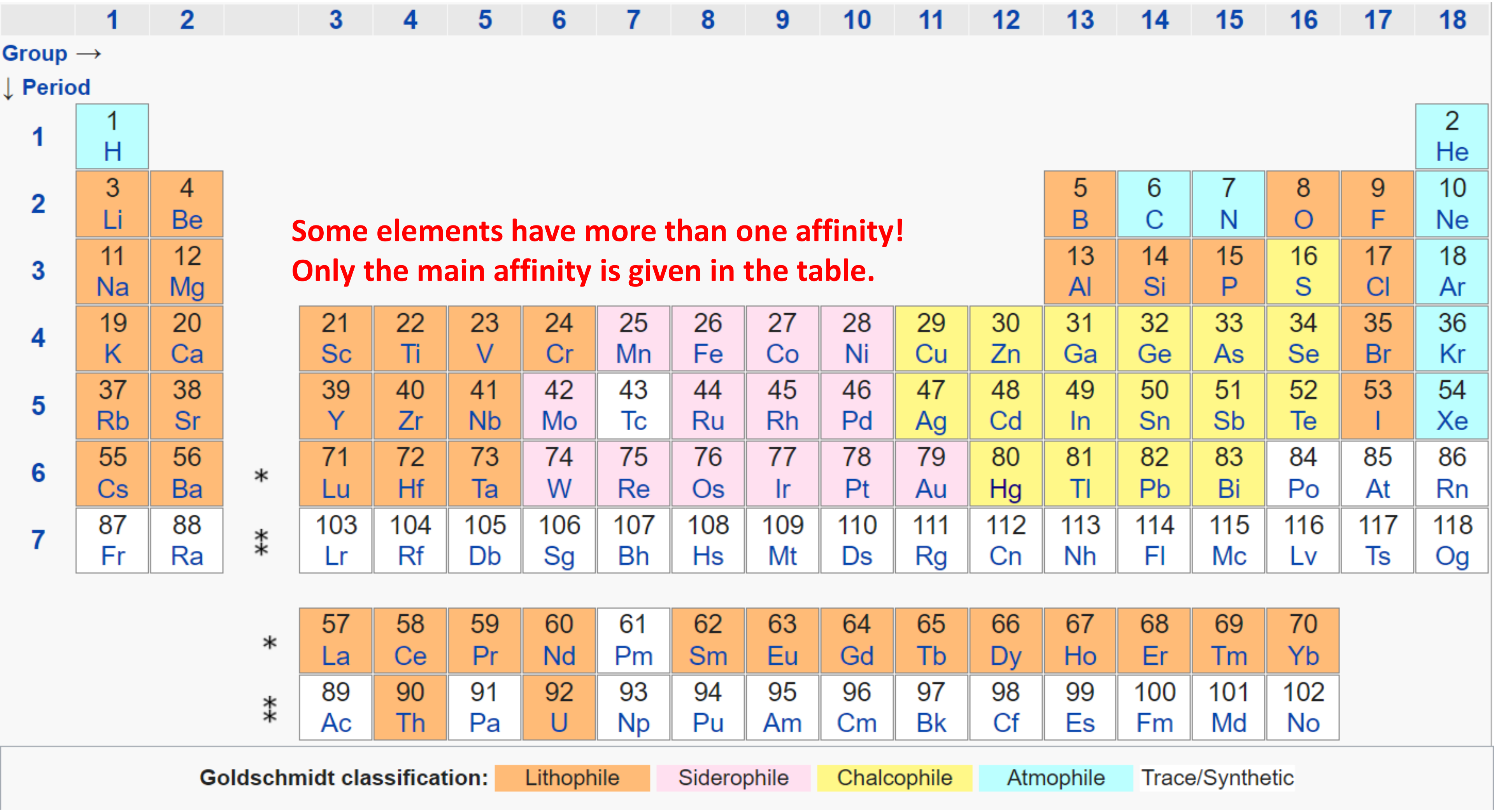
Shannon ionic radii:
O^{2-} = 140 pm
Si^{4+} = 40 pm

Order of abundance	*Element*	*Weight % in crust*	*Molar % in crust*	*Volume % in crust*	*Typical natural form at Earth surface*
1	Oxygen	46.3	60.2	**94.2**	O^{2-} in minerals and H_2O; small amount as elemental O_2 in atmosphere
2	Silicon	28.2	20.8	0.8	Almost all as Si^{4+} in silicate minerals; some as H_4SiO_4 in seawater
3	Aluminum	8.1	6.2	0.4	Almost all as Al^{3+} in minerals
4	Hydrogen	0.1	2.9	-	Almost all as H^+ in H_2O, OH^- in minerals, and HCO_3^-
5	Sodium	2.4	2.2	1.1	All as Na^+, largely in minerals but also in seawater
6	Calcium	4.1	2.1	1.2	All as Ca^{2+}, largely in minerals but also in seawater
7	Iron	5.4	2.0	0.4	Mostly as Fe^{2+} and Fe^{3+} in minerals
8	Magnesium	2.3	2.0	0.3	All as Mg^{2+}, largely in minerals but also in seawater
9	Potassium	2.1	1.1	1.5	All as K^+, largely in minerals but also in seawater
10	Titanium	0.5	0.2	0.04	Almost all as Ti^{4+} in minerals
11	Phosphorous	0.1	0.1	0.002	Mostly as P^{5+} in phosphate (PO_4^{3-})
12	Fluorine	0.06	0.07	0.1	All as F^-, largely in minerals but also in seawater
13	Carbon	0.02	0.04	0.0003	Range of valence states from 4- to 4+
14	Manganese	0.1	0.04	0.007	Mostly as Mn^{2+}, Mn^{3+}, and Mn^{4+} in minerals
15	Sulfur	0.03	0.02	0.004	Almost all as S^{6+} in sulfate (SO_4^{2-}) or S^{2-} in sulfides
. . .					
≥73	Gold	0.0000003	0.00000003	-	As Au^0 and Au^+

Percentages are calculated from data for average continental crust in Appendix III of Krauskopf (1979). For a more recent but less complete compilation, see Taylor and McLennan (1985) The abundances of the first fifteen elements listed add up to 99.77 molar % of average crust. Gold is included solely to allow comparison of these 15 most abundant elements to a very scarce element. Volume percent for oxygen in boldface illustrates the paraphrase by Mason (1958) of the words of Viktor Goldschmidt that "the lithosphere may well be called the oxysphere".

Some Fundamentals of Mineralogy and Geochemistry, L. Bruce Railsback, http://railsback.org/FundamentalsIndex.html

Goldschmidt classification (1)



Group → ↓ Period	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Some elements have more than one affinity!
Only the main affinity is given in the table.

Goldschmidt classification: Lithophile Siderophile Chalcophile Atmophile Trace/Synthetic

Figure: Wikipedia

Goldschmidt classification (2)

- **Lithophile** = rock-loving elements
  - Remain on or close to the surface because they combine readily with oxygen, forming compounds that do not sink into the core
  - The strong affinity for oxygen causes them to associate very strongly with **silica**, forming relatively low-density minerals that thus float to the crust
  - Many lithophile metals are of considerable value as structural metals (magnesium, aluminium, titanium, vanadium), but the process of smelting these metals is ***extremely energy-intensive***
- **Siderophile** = iron-loving elements
  - High-density transition metals which tend to sink into the core because they dissolve readily in iron either as solid solutions or in the molten state
  - Many siderophile elements have very small affinity for oxygen (*e.g.* gold)
  - Form stronger bonds with carbon or sulfur, but even these are not strong enough to separate out with the chalcophile elements
  - Include ***technologically highly important*** precious metals

Ref: https://en.wikipedia.org/wiki/Goldschmidt_classification

Goldschmidt classification (3)

- **Chalcophile** = chalcogen-loving / ore-loving elements
  - Remain on or close to the surface because they combine readily with sulfur and/or some other chalcogen other than oxygen, forming compounds which do not sink into the core
  - Sulfides are much denser than the silicate minerals formed by lithophile elements and chalcophile elements separated below the lithophiles at the time of the first crystallisation of the Earth's crust
  - Because the minerals they form are nonmetallic, this depletion has not reached the levels found with siderophile elements
  - Chalcophiles can be easily extracted by reduction with coke
- **Atmophile** = gas-loving (volatile) elements
  - Remain mostly on or above the surface because they are, or occur in, liquids and/or gases at temperatures and pressures found on the surface
  - Strongly depleted on earth as a whole relative to their solar abundances owing to losses from the atmosphere during the formation of the Earth
  - Carbon: CO, CO_2, hydrocarbons

Ref: https://en.wikipedia.org/wiki/Goldschmidt_classification

Structure of Earth

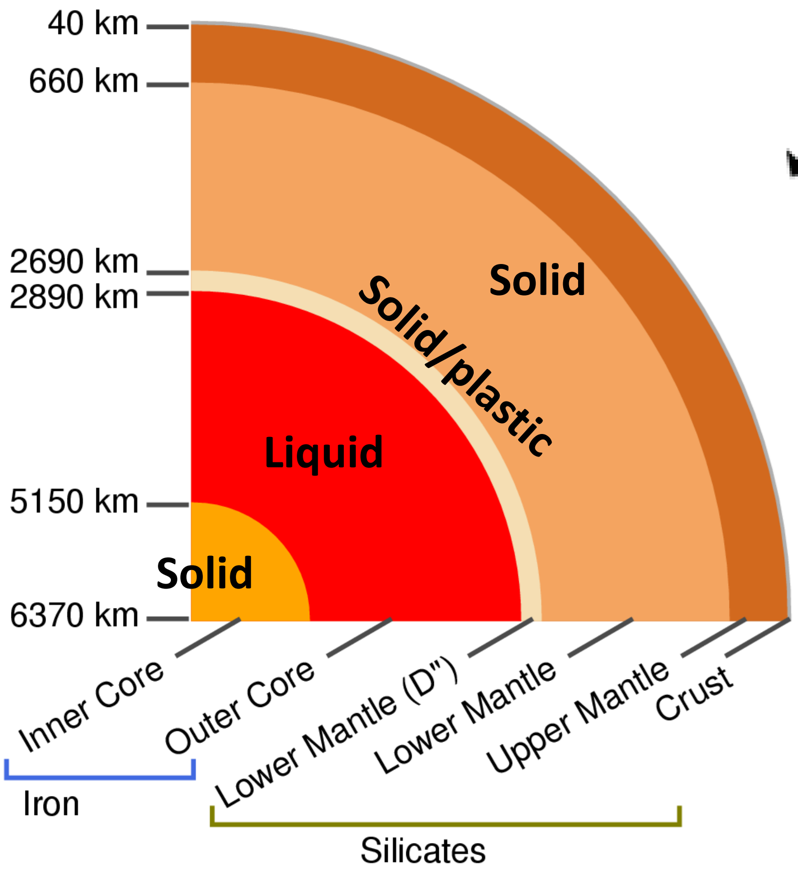


Figure: http://backreaction.blogspot.fi/2010/06/diamonds-in-earth-science.html

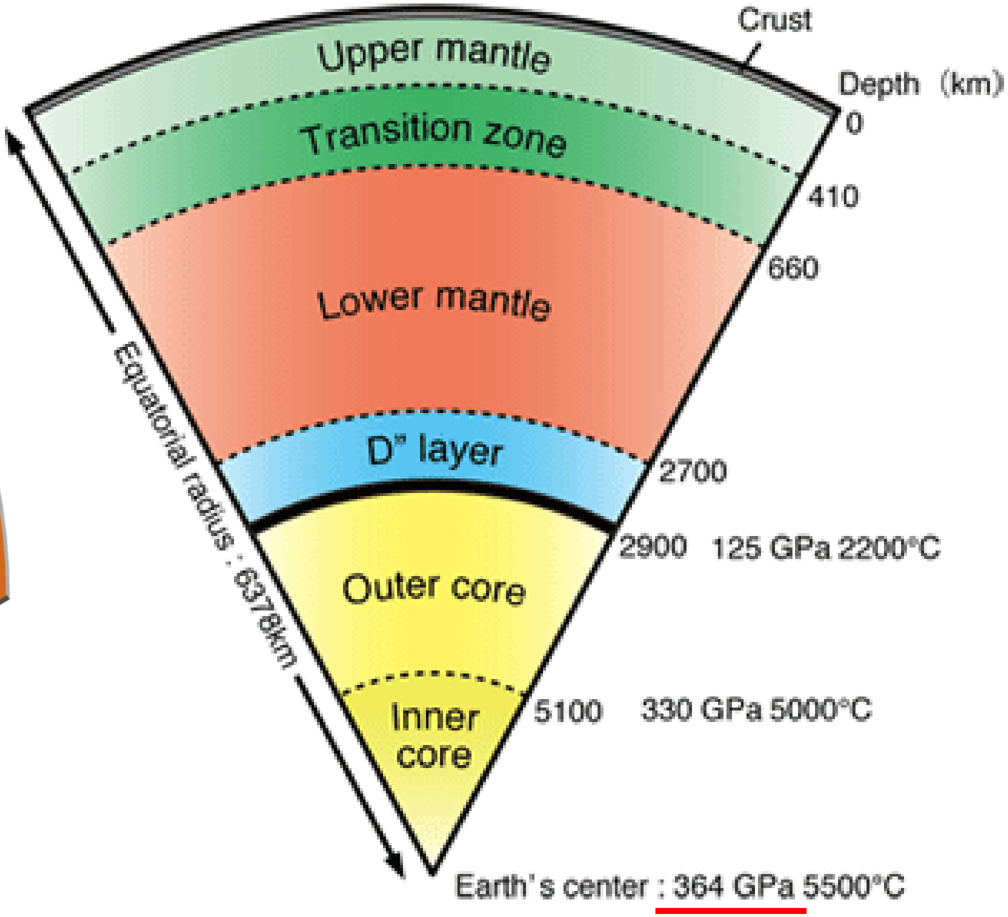


Figure: http://www.spring8.or.jp/en/news_publications/research_highlights/no_57/

Example: graphite-diamond phase transition occurs at ~130 km depth for T = 800°C

Geophysical exploration

- Seismic methods
  - Example: Reflection seismology
  - When a seismic wave travelling through the Earth encounters an interface between two materials with different acoustic impedances, some of the wave energy will **reflect** off the interface and some will **refract** through the interface
  - Seismic source: dynamite, seismic vibrator (“thumper truck”)
- Geodesy and gravity techniques
- Magnetic techniques (e.g. aeromagnetic surveys)
- Electrical and electromagnetic techniques
  - Magnetotellurics
  - Electrical resistivity tomography
  - Ground-penetrating radar
- The brute-force approach: drill a hole and explore what comes out (next slide)

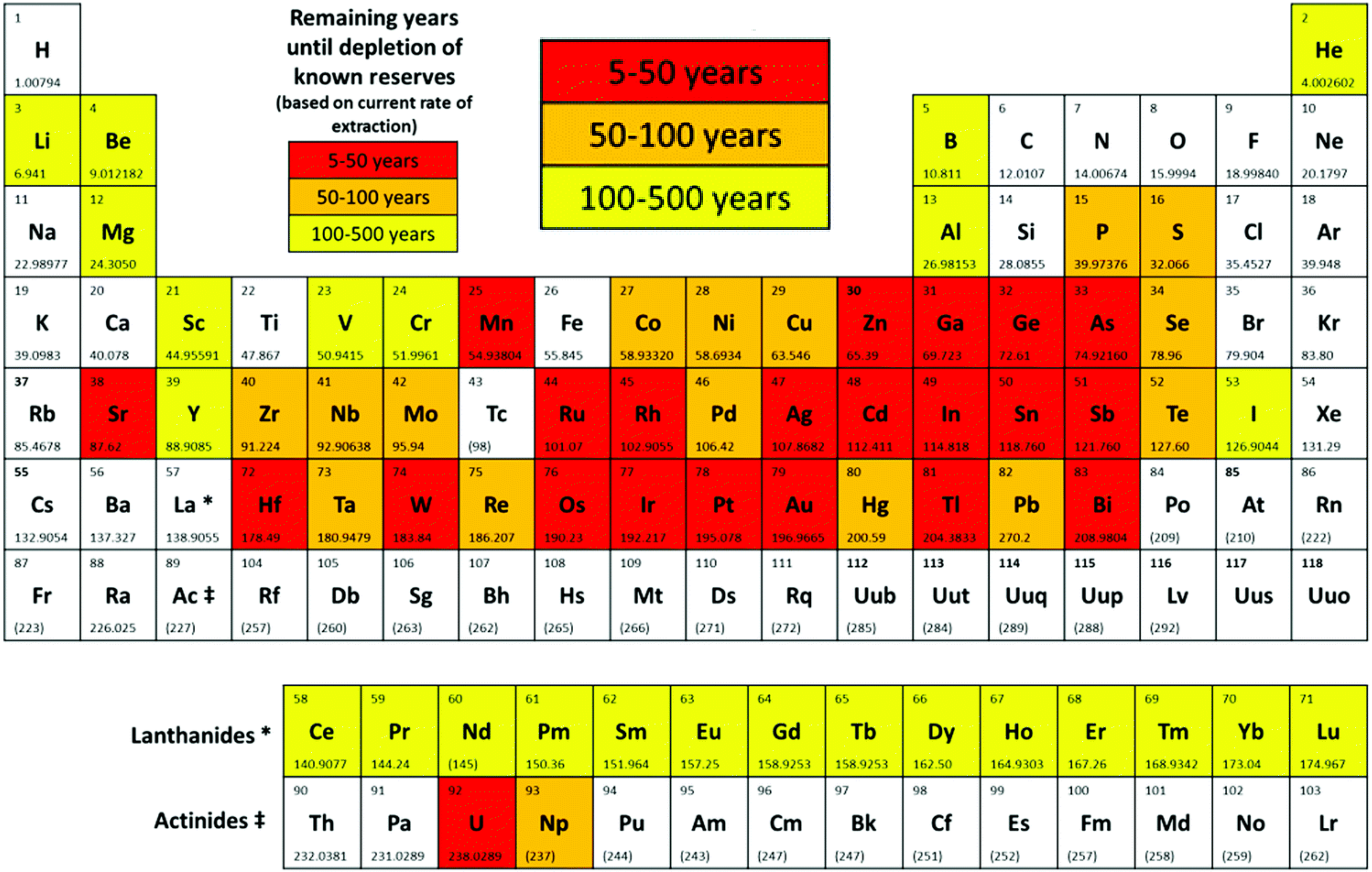
Kola Superdeep Borehole

- Drilling began in 1970, reached 12 262 meters in 1989
  - Abandoned in 2006
  - Mariana Trench: 10 994 m
- Site of fascinating geophysical discoveries, but actually reached only 1/3 of the estimated thickness of the Baltic continental crust (35 km)

The borehole, welded shut

Ref: https://en.wikipedia.org/wiki/Kola_Superdeep_Borehole

Accessibility and supply of elements (1/3)



Remaining years until depletion of known reserves
(based on current rate of extraction)

🟥 5-50 years
🟧 50-100 years
🟨 100-500 years

🟥 5-50 years
🟧 50-100 years
🟨 100-500 years

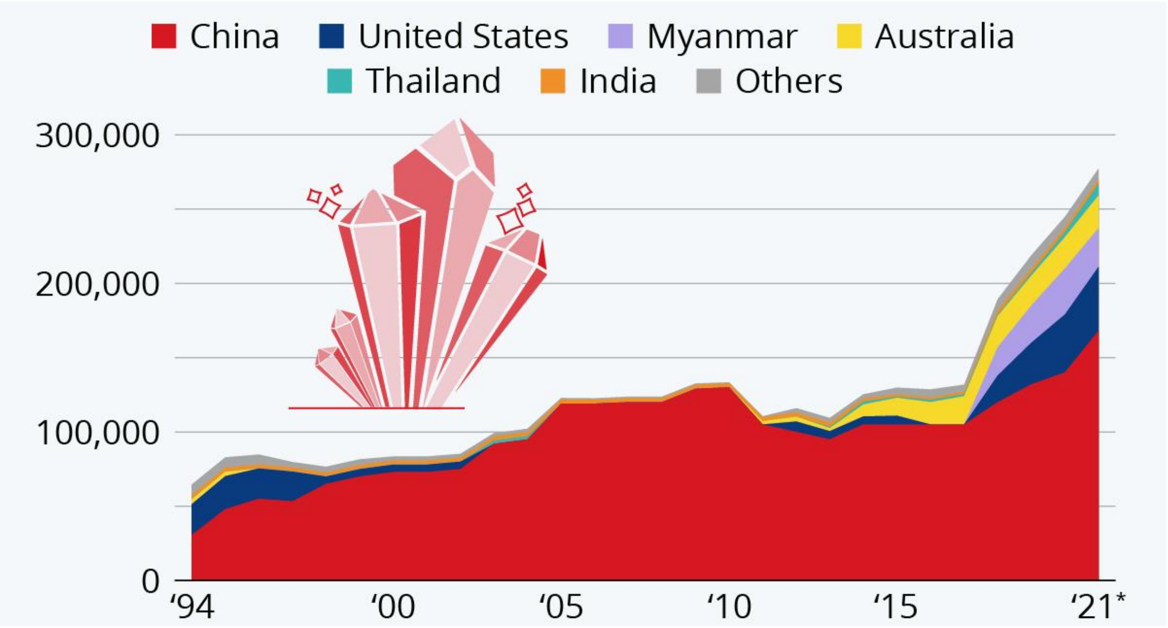
1 **H** 1.00794																	🟨 2 **He** 4.002602
🟨 3 **Li** 6.941	🟨 4 **Be** 9.012182											🟨 5 **B** 10.811	6 **C** 12.0107	7 **N** 14.00674	8 **O** 15.9994	9 **F** 18.99840	10 **Ne** 20.1797
11 **Na** 22.98977	🟨 12 **Mg** 24.3050											🟨 13 **Al** 26.98153	14 **Si** 28.0855	🟧 15 **P** 39.97376	🟧 16 **S** 32.066	17 **Cl** 35.4527	18 **Ar** 39.948
19 **K** 39.0983	20 **Ca** 40.078	🟨 21 **Sc** 44.95591	22 **Ti** 47.867	🟨 23 **V** 50.9415	🟨 24 **Cr** 51.9961	🟥 25 **Mn** 54.93804	26 **Fe** 55.845	🟧 27 **Co** 58.93320	🟧 28 **Ni** 58.6934	🟧 29 **Cu** 63.546	🟥 30 **Zn** 65.39	🟥 31 **Ga** 69.723	🟥 32 **Ge** 72.61	🟥 33 **As** 74.92160	🟧 34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
37 **Rb** 85.4678	🟥 38 **Sr** 87.62	🟨 39 **Y** 88.9085	🟧 40 **Zr** 91.224	🟧 41 **Nb** 92.90638	🟧 42 **Mo** 95.94	43 **Tc** (98)	🟥 44 **Ru** 101.07	🟥 45 **Rh** 102.9055	🟧 46 **Pd** 106.42	🟥 47 **Ag** 107.8682	🟥 48 **Cd** 112.411	🟥 49 **In** 114.818	🟥 50 **Sn** 118.760	🟥 51 **Sb** 121.760	🟧 52 **Te** 127.60	🟨 53 **I** 126.9044	54 **Xe** 131.29
55 **Cs** 132.9054	56 **Ba** 137.327	57 **La** * 138.9055	🟥 72 **Hf** 178.49	🟧 73 **Ta** 180.9479	🟥 74 **W** 183.84	🟧 75 **Re** 186.207	🟥 76 **Os** 190.23	🟥 77 **Ir** 192.217	🟥 78 **Pt** 195.078	🟥 79 **Au** 196.9665	🟧 80 **Hg** 200.59	🟥 81 **Tl** 204.3833	🟧 82 **Pb** 270.2	🟥 83 **Bi** 208.9804	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.025	89 **Ac** ‡ (227)	104 **Rf** (257)	105 **Db** (260)	106 **Sg** (263)	107 **Bh** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Ds** (271)	111 **Rq** (272)	112 **Uub** (285)	113 **Uut** (284)	114 **Uuq** (289)	115 **Uup** (288)	116 **Lv** (292)	117 **Uus**	118 **Uuo**

Lanthanides *	🟨 58 **Ce** 140.9077	🟨 59 **Pr** 144.24	🟨 60 **Nd** (145)	🟨 61 **Pm** 150.36	🟨 62 **Sm** 151.964	🟨 63 **Eu** 157.25	🟨 64 **Gd** 158.9253	🟨 65 **Tb** 158.9253	🟨 66 **Dy** 162.50	🟨 67 **Ho** 164.9303	🟨 68 **Er** 167.26	🟨 69 **Tm** 168.9342	🟨 70 **Yb** 173.04	🟨 71 **Lu** 174.967
Actinides ‡	90 **Th** 232.0381	91 **Pa** 231.0289	🟥 92 **U** 238.0289	🟧 93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

Ref: A. J. Hunt, T. J. Farmer and J. H. Clark, in *Element Recovery and Sustainability*, ed. A. J. Hunt, Royal Society of Chemistry, London, **2013**, ch. 1, pp. 1–28

Accessibility and supply of elements (2/3)

- The crustal abundance of elements is not equal to their accessibility
  - Elements are not equally distributed throughout the Earth
- Some elements have been declared to be [Critical Raw Materials]() (CRM) by EU
- For example, Rare Earth Elements (REE) are often discussed as critical in supply
  - For REE, it is actually a question of supply and demand
  - In 2011, there was a steep increase in prices
  - New mining operations have been opened around the world after that
- So far, new supply of elements has emerged when the price has been right



Global mine production of rare earth elements ([statista.com]()). Documented production only.

Source: United States Geological Survey
License: CC-BY-ND

*Estimate

Accessibility and supply of elements (3/3)

- The key question is, should we really push to find more elements at any cost?
    - Enviromental problems become more severe as previously inaccessible resources are being utilized
    - Minerals are one of the most important reasons to human conflicts (for example, Democratic Republic of the Congo)
    - It is not sensible to use easily accessible resources for non-recyclable use-once-throw-away consumer goods and leave no reserves for the future
- Possible remedies:
    1. Plan the use of resources in a better way
    2. Improve recycling/re-use
    3. Substitute Critical Raw Materials with new functional materials
- All these solutions require **chemists** and **materials scientists**!

Minerals

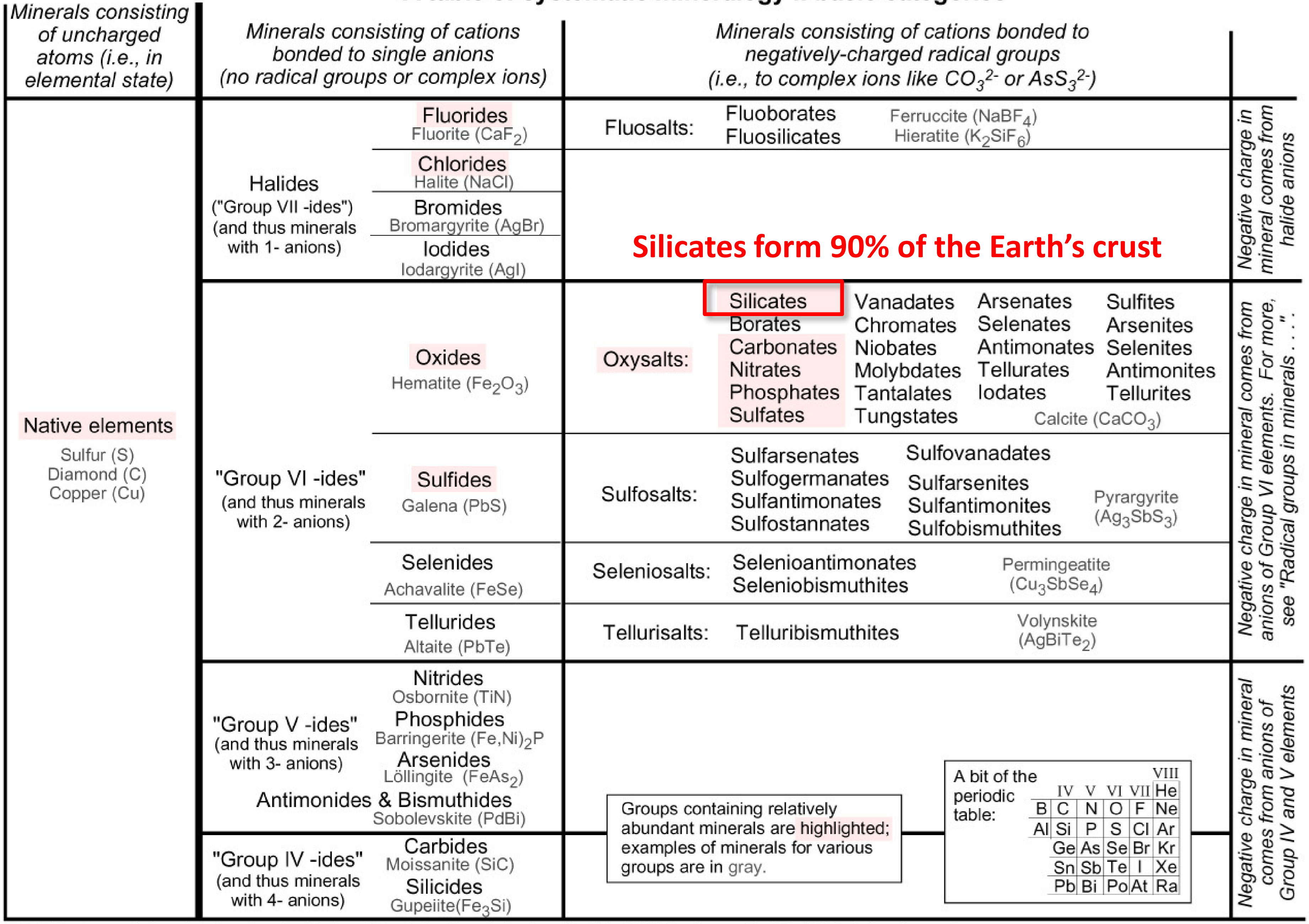
Minerals

- 1995 definition of a **mineral** from The International Association of Minerals (IMA):
  - "A mineral is an element or chemical compound that is normally crystalline and that has been formed as a result of geological processes“
- More detailed (and controversial) definition (Tasa 2007):
  1. Naturally occurring
  2. Stable at room temperature
  3. Represented by a chemical formula (*note: many are solid solutions*!)
  4. Usually abiogenic (not resulting from the activity of living organisms)
  5. Ordered atomic arrangement
- IMA has approved over 5500 minerals (2020)

Mineral-related databases

- IMA Database of Mineral Properties: http://rruff.info/ima/
  - For instructions, see MyCourses -> Databases -> IMA documentation
- The RRUFF™ Project: http://rruff.info
  - Integrated database of Raman spectra, X-ray diffraction and chemistry data for minerals (> 20 000 Raman spectra)
  - For instructions, see MyCourses -> Databases -> RRUFF documentation
- American Mineralogist Crystal Structure Database (AMSCSD)
  - Over 4000 crystal structures
  - Shortcut to all structures: http://rruff.geo.arizona.edu/AMS/all_minerals.php
- Minerals are a popular topic and hence Wikipedia is also an excellent resource
  - https://en.wikipedia.org/wiki/Category:Minerals_by_crystal_system

A table of systematic mineralogy I: basic categories



Minerals consisting of uncharged atoms (i.e., in elemental state)	*Minerals consisting of cations bonded to single anions (no radical groups or complex ions)*		*Minerals consisting of cations bonded to negatively-charged radical groups (i.e., to complex ions like CO_3^{2-} or AsS_3^{2-})*			
Native elements Sulfur (S) Diamond (C) Copper (Cu)	Halides ("Group VII -ides") (and thus minerals with 1- anions)	Fluorides Fluorite (CaF_2)	Fluosalts:	Fluoborates Fluosilicates	Ferruccite ($NaBF_4$) Hieratite (K_2SiF_6)	*Negative charge in mineral comes from halide anions*
		Chlorides Halite (NaCl)	**Silicates form 90% of the Earth's crust**			
		Bromides Bromargyrite (AgBr)				
		Iodides Iodargyrite (AgI)				
	"Group VI -ides" (and thus minerals with 2- anions)	Oxides Hematite (Fe_2O_3)	Oxysalts:	Silicates Borates Carbonates Nitrates Phosphates Sulfates Vanadates Chromates Niobates Molybdates Tantalates Tungstates Arsenates Selenates Antimonates Tellurates Iodates Sulfites Arsenites Selenites Antimonites Tellurites	Calcite ($CaCO_3$)	*Negative charge in mineral comes from anions of Group VI elements. For more, see "Radical groups in minerals . . . ."*
		Sulfides Galena (PbS)	Sulfosalts:	Sulfarsenates Sulfogermanates Sulfantimonates Sulfostannates Sulfovanadates Sulfarsenites Sulfantimonites Sulfobismuthites	Pyrargyrite (Ag_3SbS_3)	
		Selenides Achavalite (FeSe)	Seleniosalts:	Selenioantimonates Seleniobismuthites	Permingeatite (Cu_3SbSe_4)	
		Tellurides Altaite (PbTe)	Tellurisalts:	Telluribismuthites	Volynskite ($AgBiTe_2$)	
	"Group V -ides" (and thus minerals with 3- anions)	Nitrides Osbornite (TiN) Phosphides Barringerite $(Fe,Ni)_2P$ Arsenides Löllingite ($FeAs_2$) Antimonides & Bismuthides Sobolevskite (PdBi)				*Negative charge in mineral comes from anions of Group IV and V elements*
	"Group IV -ides" (and thus minerals with 4- anions)	Carbides Moissanite (SiC) Silicides Gupeiite(Fe_3Si)				

Groups containing relatively abundant minerals are highlighted; examples of minerals for various groups are in gray.

A bit of the periodic table:

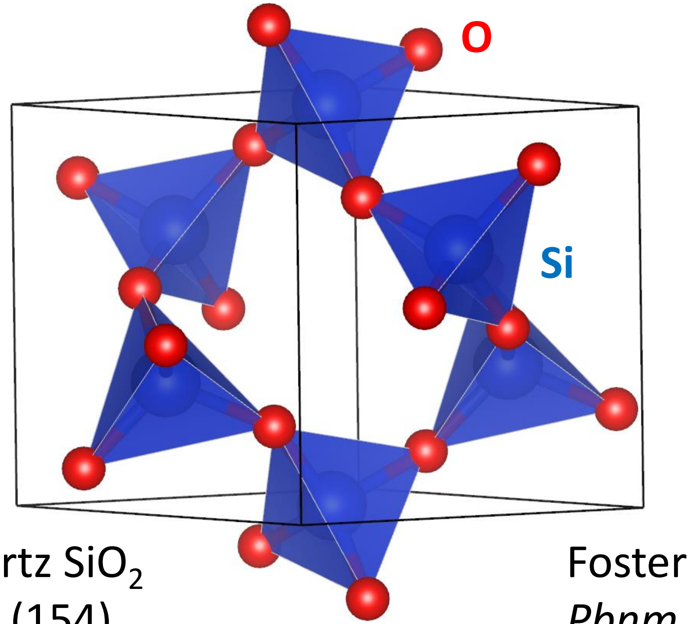
	IV	V	VI	VII	VIII
					He
B	C	N	O	F	Ne
Al	Si	P	S	Cl	Ar
	Ge	As	Se	Br	Kr
	Sn	Sb	Te	I	Xe
	Pb	Bi	Po	At	Ra

This table does not show hybrid categories that would include minerals like brenkite ($Ca_2CO_3F_2$) or kermesite (Sb_2S_2O). It also does not show H^+-bearing minerals; their inclusion would best be shown with a third dimension leading to hydroxides, bicarbonates, bisulfates, etc.

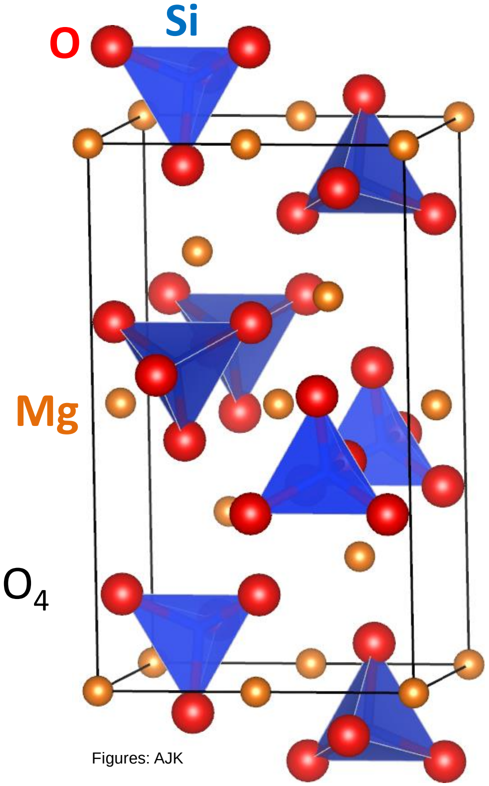
LBR SystematicMinTable10, 11/2007

Some Fundamentals of Mineralogy and Geochemistry, L. Bruce Railsback, http://railsback.org/FundamentalsIndex.html

Silicates



α-quartz SiO_2
$P3_221$ (154)

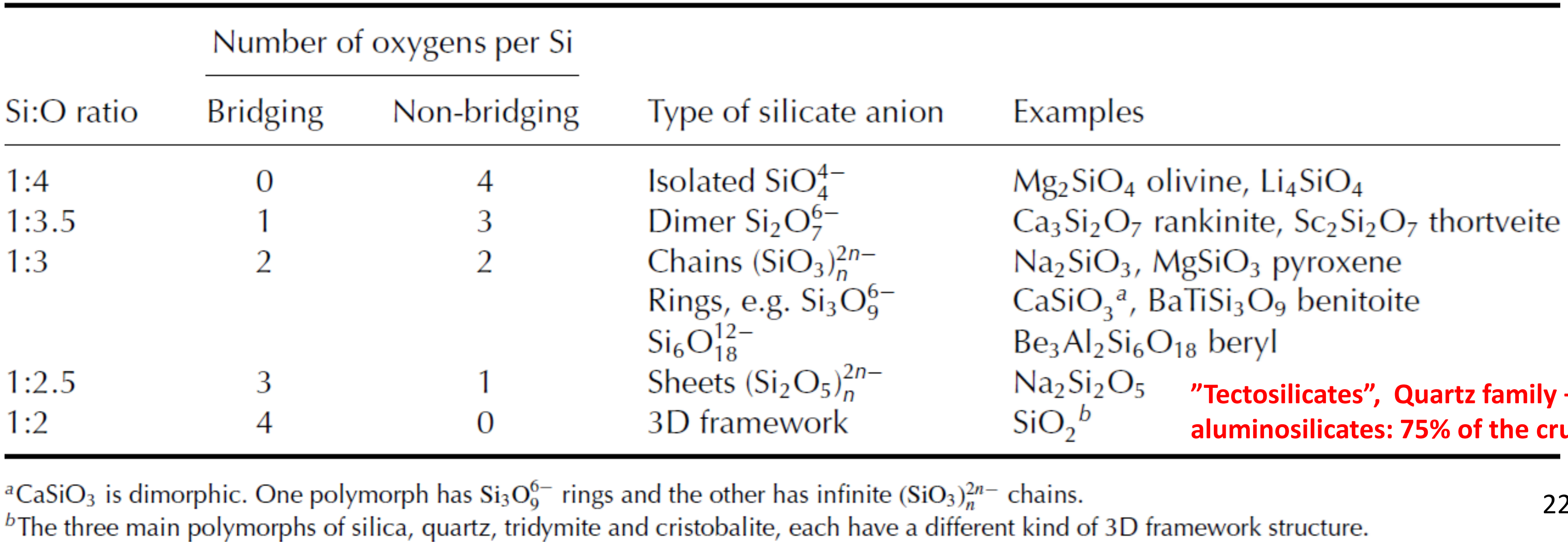


Fosterite Mg_2SiO_4
Pbnm (62)

Figures: AJK

Ref: West p. 81

Table 1.27 ***Relation between chemical formula and silicate anion structure***



	Number of oxygens per Si			
Si:O ratio	Bridging	Non-bridging	Type of silicate anion	Examples
1:4	0	4	Isolated SiO_4^{4-}	Mg_2SiO_4 olivine, Li_4SiO_4
1:3.5	1	3	Dimer $Si_2O_7^{6-}$	$Ca_3Si_2O_7$ rankinite, $Sc_2Si_2O_7$ thortveite
1:3	2	2	Chains $(SiO_3)_n^{2n-}$	Na_2SiO_3, $MgSiO_3$ pyroxene
			Rings, e.g. $Si_3O_9^{6-}$	$CaSiO_3$[a], $BaTiSi_3O_9$ benitoite
			$Si_6O_{18}^{12-}$	$Be_3Al_2Si_6O_{18}$ beryl
1:2.5	3	1	Sheets $(Si_2O_5)_n^{2n-}$	$Na_2Si_2O_5$
1:2	4	0	3D framework	SiO_2[b]

"Tectosilicates", Quartz family + aluminosilicates: 75% of the crust

[a] $CaSiO_3$ is dimorphic. One polymorph has $Si_3O_9^{6-}$ rings and the other has infinite $(SiO_3)_n^{2n-}$ chains.
[b] The three main polymorphs of silica, quartz, tridymite and cristobalite, each have a different kind of 3D framework structure.

Aluminosilicates: Feldspars

- By far the most abundant group of minerals in the earth's crust, forming about 60% of terrestrial rocks

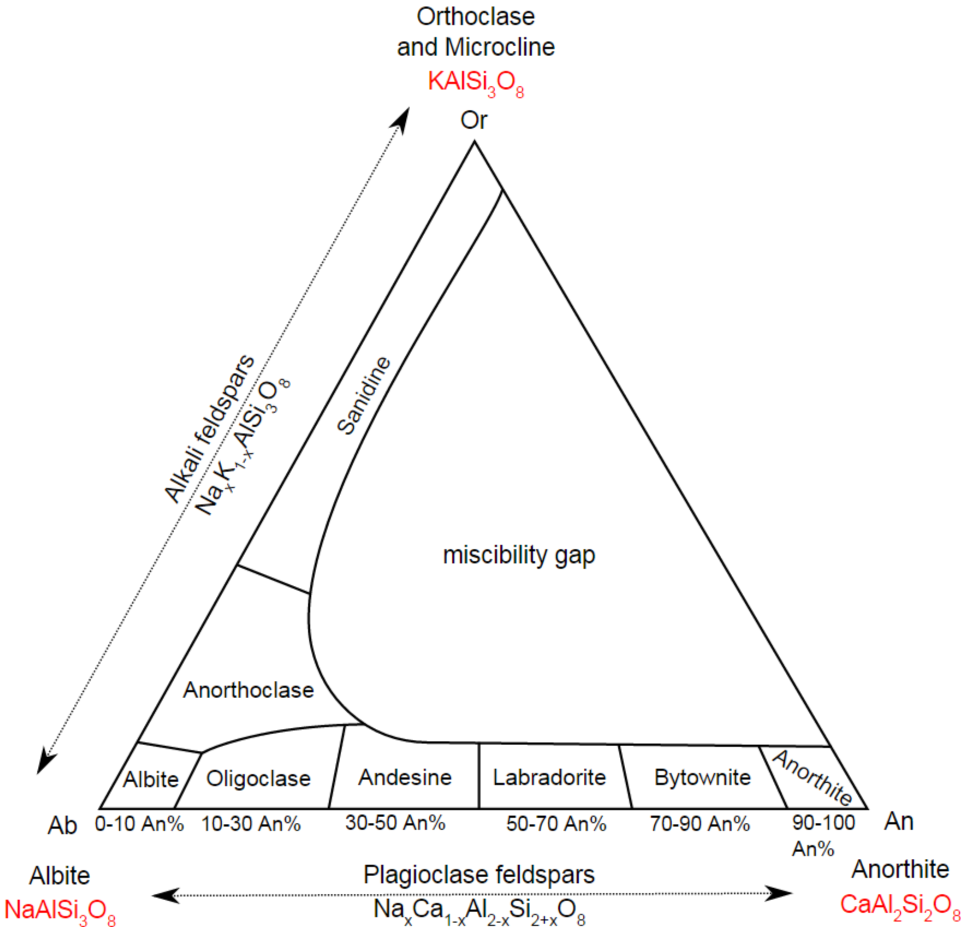


Figure: Wikipedia

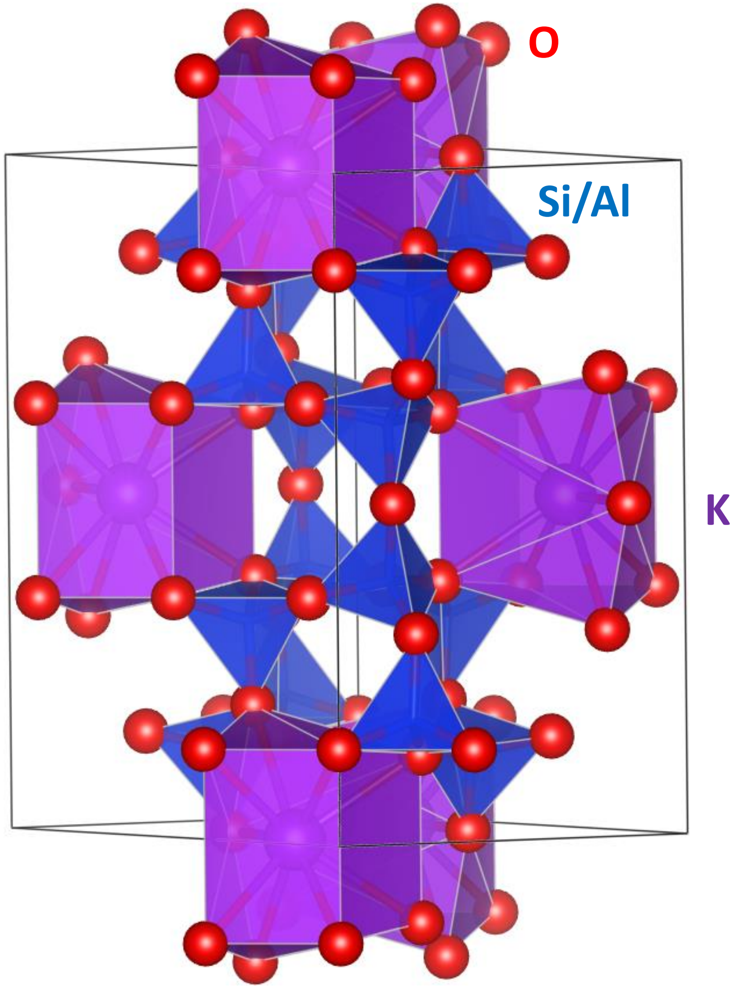


Figure: AJK

Feldspar $K(AlSi_3O_8)$
C 1 2/*m* (12)

Aluminosilicates: Zeolites

- Microporous aluminosilicate minerals
  - Cronstedt 1756: heating ***stilbite***, $NaCa_4(Si_{27}Al_9)O_{72}\cdot 28(H_2O)$, produced steam
  - *Zéō* -> to boil
  - *Líthos* -> rock
- Can be considered as molecular sieves, with actual industrial applications in:
  - Ion-exhange (e.g. water purification and softening)
  - Catalysis (e.g. In petrochemical industry)
- http://www.iza-structure.org/databases/
- http://www.hypotheticalzeolites.net/

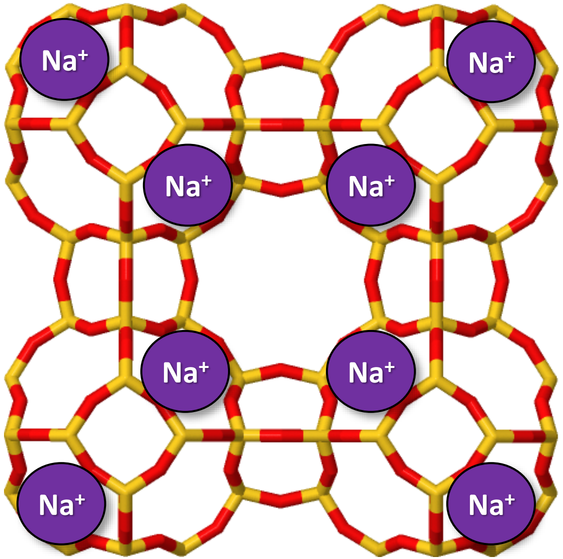


Figure: AJK

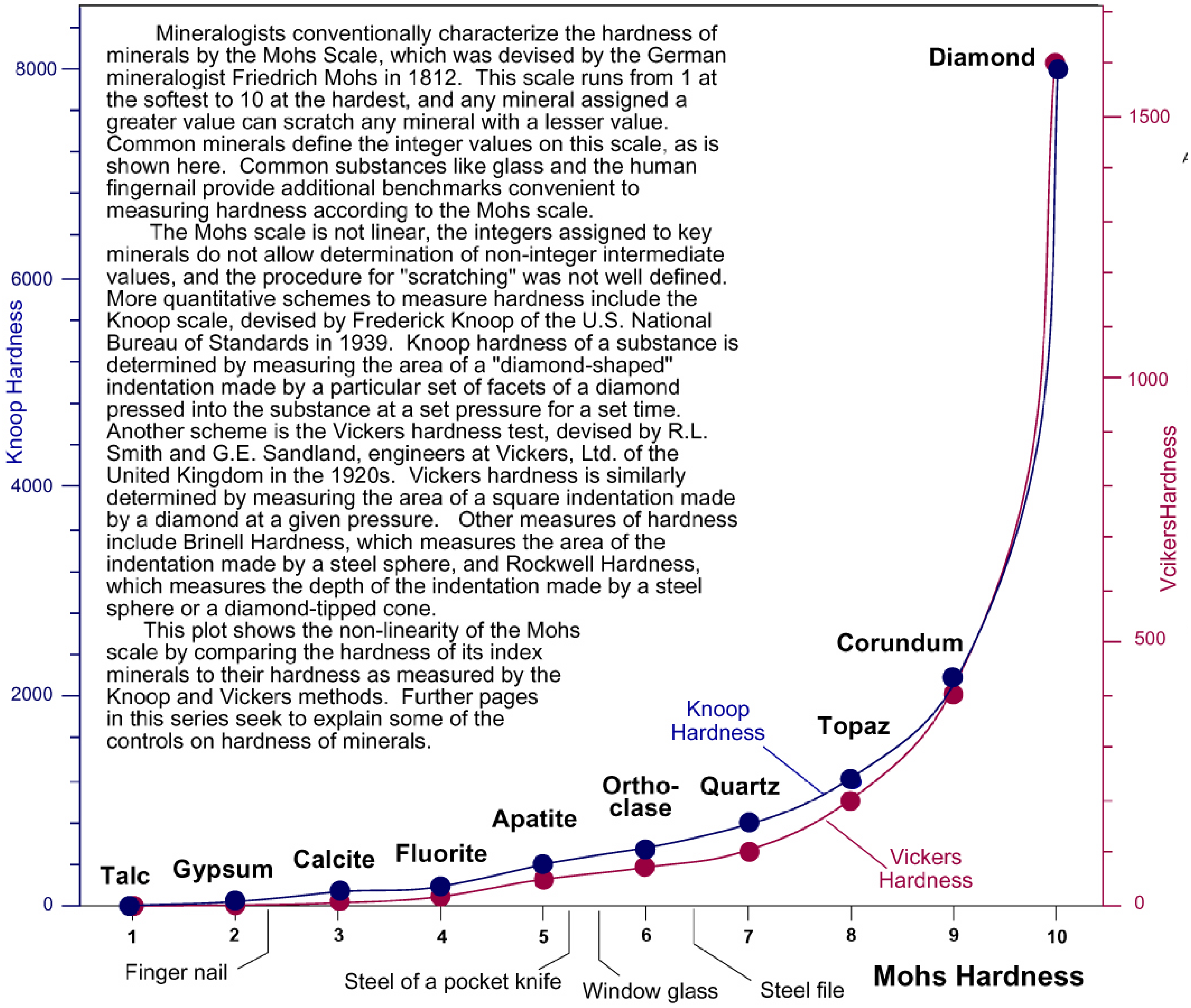
LTA zeolite (*Pm*-3*m*)
$[Na_{12}(H_2O)_{27}]_8[Al_{12}Si_{12}\,O_{48}]_8$

Ref: https://en.wikipedia.org/wiki/Zeolite

Hardness of minerals as an example of physical property trends

Hardness of minerals I: the Mohs scale

A K



Mineralogists conventionally characterize the hardness of minerals by the Mohs Scale, which was devised by the German mineralogist Friedrich Mohs in 1812. This scale runs from 1 at the softest to 10 at the hardest, and any mineral assigned a greater value can scratch any mineral with a lesser value. Common minerals define the integer values on this scale, as is shown here. Common substances like glass and the human fingernail provide additional benchmarks convenient to measuring hardness according to the Mohs scale.

The Mohs scale is not linear, the integers assigned to key minerals do not allow determination of non-integer intermediate values, and the procedure for "scratching" was not well defined. More quantitative schemes to measure hardness include the Knoop scale, devised by Frederick Knoop of the U.S. National Bureau of Standards in 1939. Knoop hardness of a substance is determined by measuring the area of a "diamond-shaped" indentation made by a particular set of facets of a diamond pressed into the substance at a set pressure for a set time. Another scheme is the Vickers hardness test, devised by R.L. Smith and G.E. Sandland, engineers at Vickers, Ltd. of the United Kingdom in the 1920s. Vickers hardness is similarly determined by measuring the area of a square indentation made by a diamond at a given pressure. Other measures of hardness include Brinell Hardness, which measures the area of the indentation made by a steel sphere, and Rockwell Hardness, which measures the depth of the indentation made by a steel sphere or a diamond-tipped cone.

This plot shows the non-linearity of the Mohs scale by comparing the hardness of its index minerals to their hardness as measured by the Knoop and Vickers methods. Further pages in this series seek to explain some of the controls on hardness of minerals.

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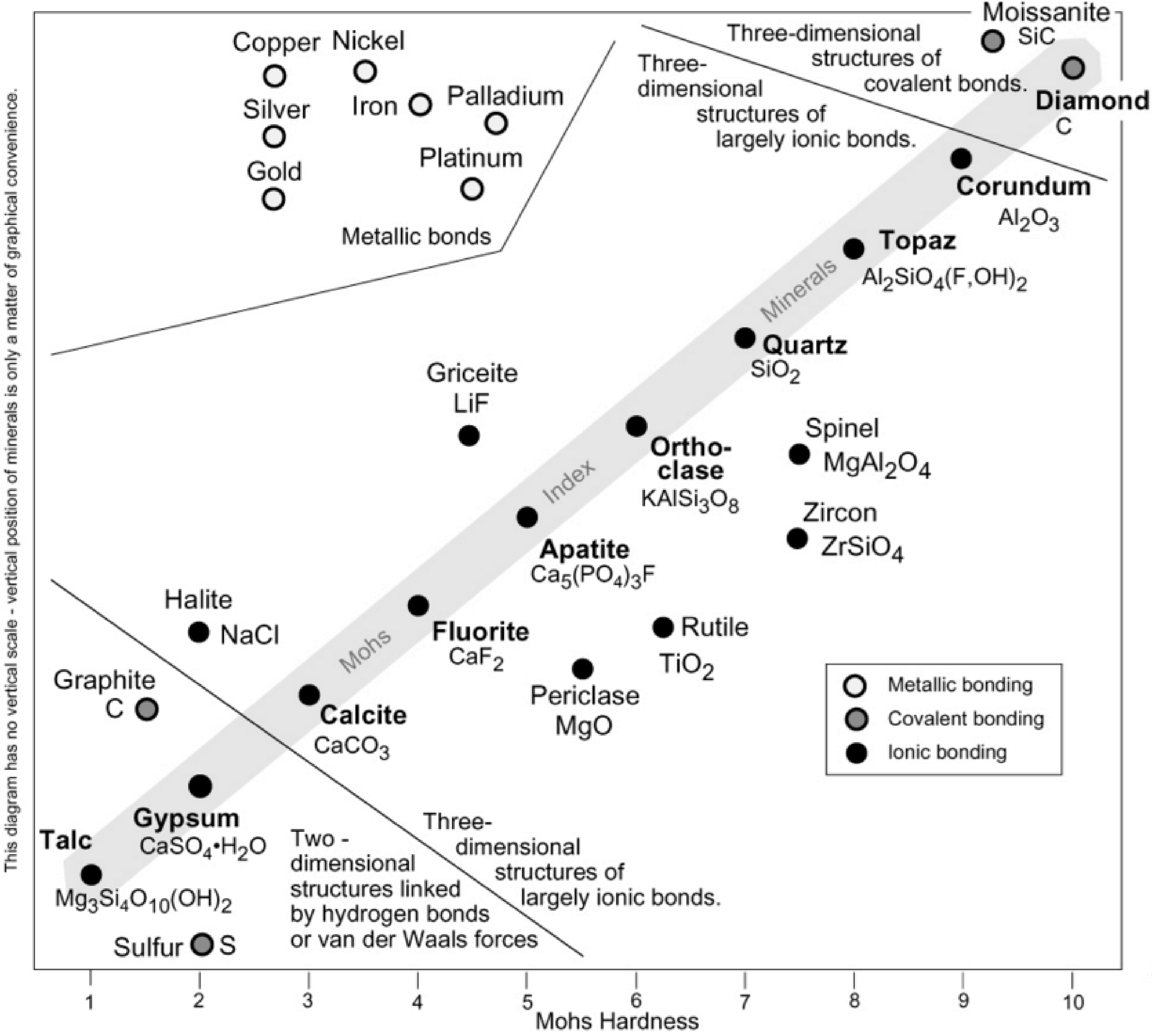
Hardness of minerals II: variation with bonding and structure



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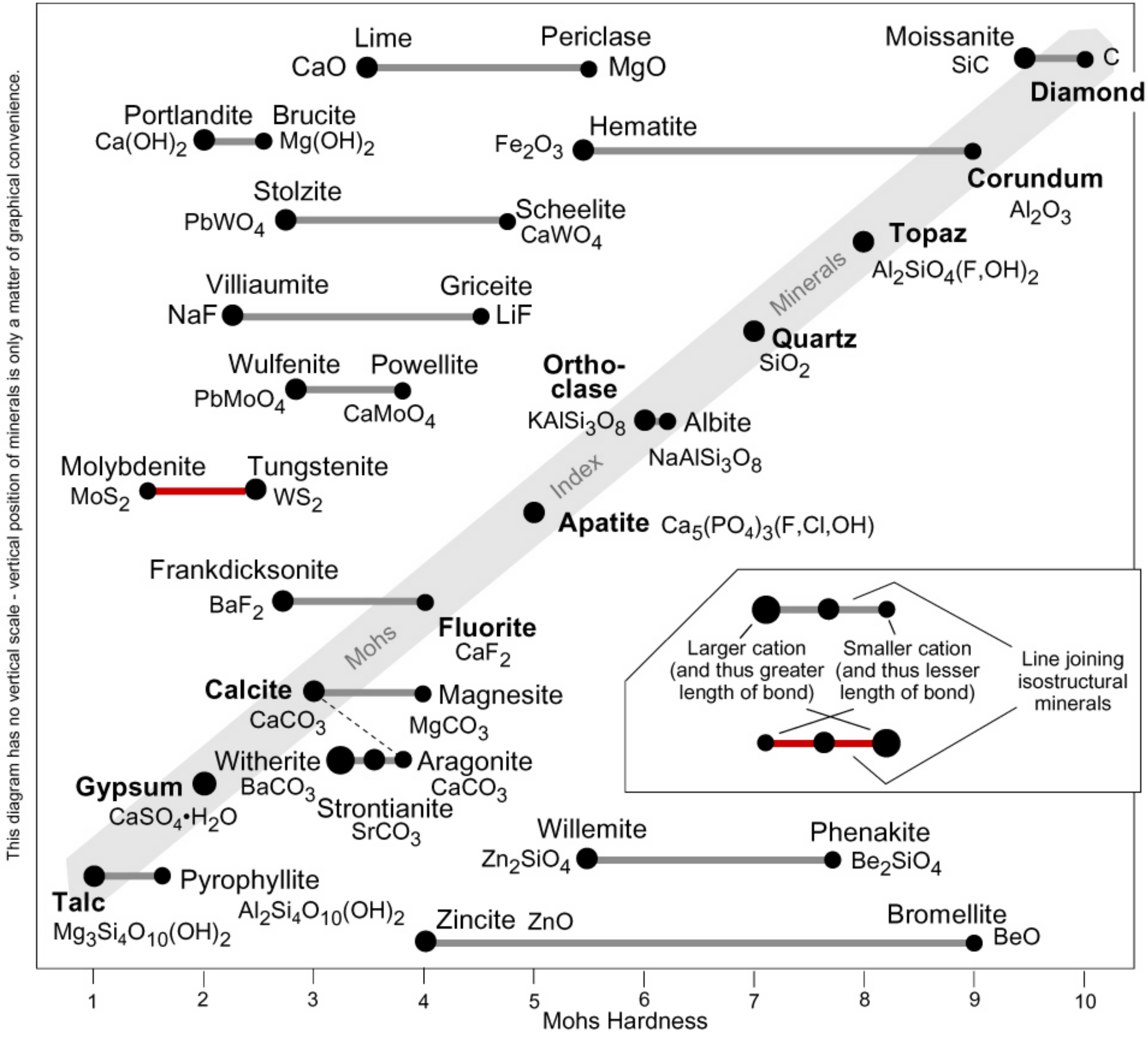
Hardness of minerals IVa: variation with bond length and cation size



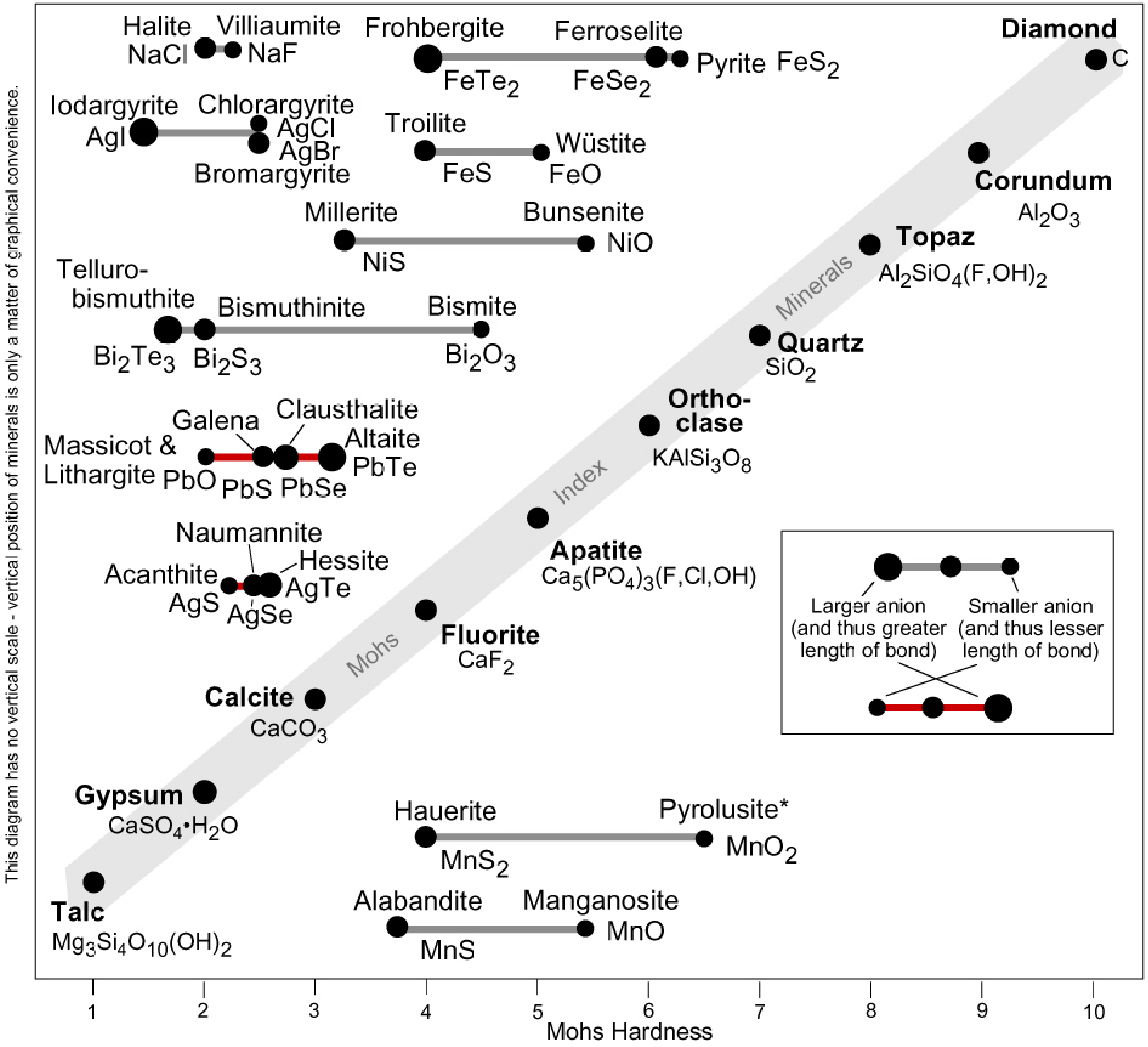
One control on hardness of a mineral is the length of bonds within that mineral. To illustrate this point, this diagram shows pairs or sets of isostructural minerals. In almost all of the examples shown on this diagram, minerals with larger cations, and thus greater bond lengths, are softer than their counterparts with smaller cations and thus shorter bonds. Much the same point can be made with regard to anion size, as is shown in Part IVb of this series.

One pair of isostructural minerals shown here, the one joined by a red line, has hardnesses opposite the pattern described above. Those minerals are molybdenite and tungstenite, the sulfides of the relatively soft cations Mo^{4+} and W^{4+}. Bonding in these two minerals may be sufficiently covalent, and bonding in tungstenite more covalent, that the more covalent bond causes greater hardness of tungstenite. The same sort of trend can be seen with regard to Ag^{+} and Pb^{2+} minerals in Part IVb of this series.

Hardness data are from Nickel, E.H., and Nichols, M.C., 1991, *Mineral Reference Manual:* New York, Van Nostrand Reinhold, 250 p.

LBR HardnessTrends29 1/2008

Hardness of minerals IVb: variation with bond length and anion size



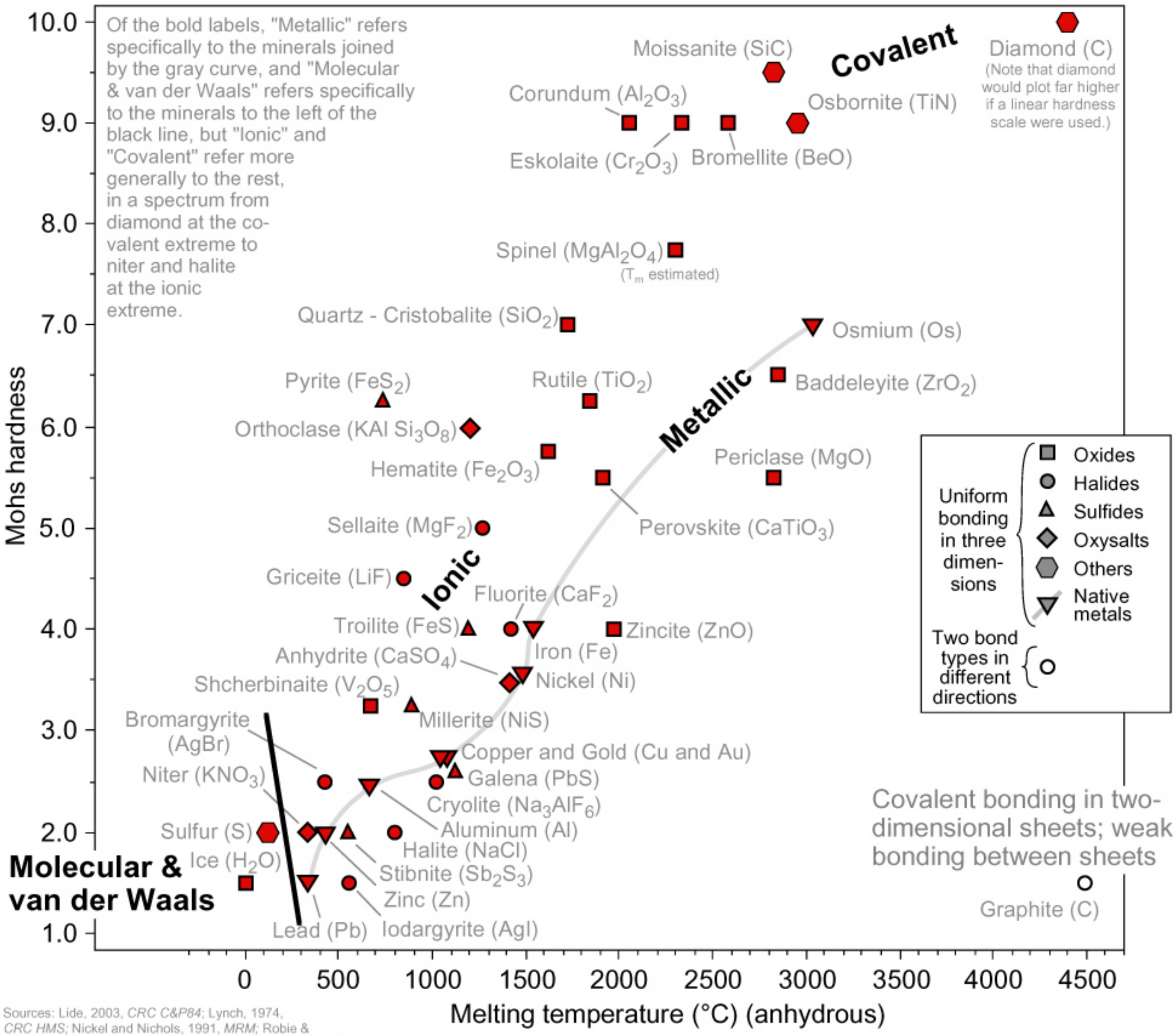
One control on the hardness of a mineral is the length of bonds within that mineral. To illustrate this point, this diagram shows pairs of chemically analogous minerals that differ only in their anions. In most of the examples shown on this diagram (the ones joined by light gray lines), minerals with larger anions, and thus greater bond lengths, are softer than their counterparts with smaller anions and thus shorter bonds.

However, in two cases shown here (the ones joined by red lines), larger anions lead to harder minerals. These are the examples where soft cations, Ag^+ and Pb^{2+}, bond to 2- anions. In these cases, the bonds of soft cations to increasingly large and thus increasingly soft anions may lead to sufficiently covalent bonds to cause greater hardness of minerals.

Hardness data are from Nickel, E.H., and Nichols, M.C., 1991, *Mineral Reference Manual:* New York, Van Nostrand Reinhold, 250 p.

* The hardness of pyrolusite is commonly listed as 2, but that is the value for earthy masses of minute crystals. The hardness of a single crystal of pyrolusite is 6.5 (Gaines et al., 1997, *Dana's New Mineralogy:* New York, John Wiley & Sons, 1819 p.).

Melting temperature and hardness of minerals



Sources: Lide, 2003, *CRC CP84;* Lynch, 1974, *CRC HMS;* Nickel and Nichols, 1991, *MRM;* Robie & Hemingway, 1995, *USGS 2131;* Strunz and Nickel, 2001, *SMT.*

The plot at left shows that there is a general correlation between melting temperature of minerals and their hardness. This relationship is most striking for the native metals, which are connected by a curve here. However, the correlation holds for all the minerals shown with filled symbols ($r^2 = 0.733$).

The reason for this relationship is that both melting temperature (a measure of susceptibility to thermal destruction) and hardness (a measure of susceptibility to mechanical destruction) depend on bond strength. Minerals with three-dimensional frameworks of covalent bonds have great hardness and high melting temperatures; diamond is the ultimate example. At the other extreme, minerals of molecules held together by weak bonds like van der Waals forces (for sulfur) and hydrogen bonds (the molecular bond for ice) have low hardness and melting temperature.

Graphite falls off this trend, for good reason. Its strong covalent bonds in two dimensions preclude disintegration and melting except at extremely high temperature, but the weak bonds between sheets (i.e., in the third dimension) allow mechanical deformation that we recognize as a low hardness.

LBR HardnessMeltingPlot06 2/2008