

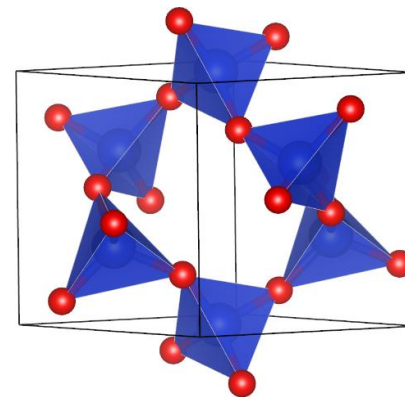
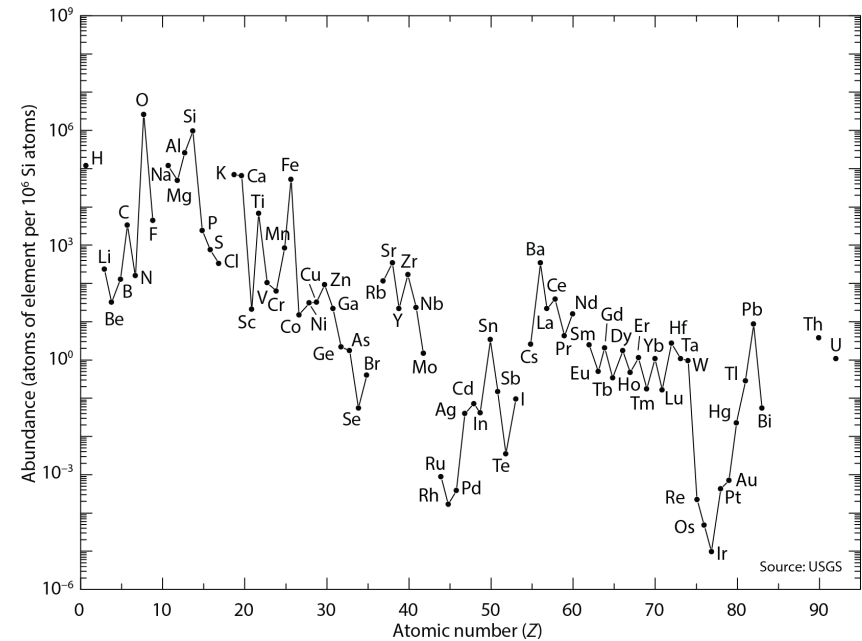
Mid-course checkpoint

Week	Lect.	Date	Topic
1: Structure	1	25.2.	Structure of crystalline materials. X-ray diffraction. Symmetry.
	2	26.2.	Structural databases, visualization of crystal structures.
2: Bonding	3	4.3.	Bonding in solids. Description of crystal structures.
	4	5.3.	Band theory. Band structures.
3: Synthesis	5	11.3.	Solid state synthesis. Phase diagrams.
	6	12.3.	High-pressure synthesis, crystal growth, thin films.
4: Characterization	7	18.3.	XRD, Miller indices. Powder XRD databases. Microscopies
	8	19.3.	Spectroscopies and thermal analysis.
5: Main groups	9	25.3.	Abundance of elements, geochemistry, minerals.
	10	26.3.	Main group compounds, allotropes, Zintl phases.
6: <i>d</i>-block metals	11	1.4.	<i>d</i> -block metals, ligand field theory, magnetism.
	12	2.4.	<i>d</i> -block metal oxides and other compounds.
7: Specialized topics I	13	15.4.	Defects, non-stoichiometric oxides.
	14	16.4.	Semiconductors, doping, electrical properties.
8: Specialized topics II	15	23.4.	Tuesday. Layered compounds, intercalation chemistry, diffusion in solids.
	16	24.4.	Wednesday. Summary of all course topics. Project work checkpoint.

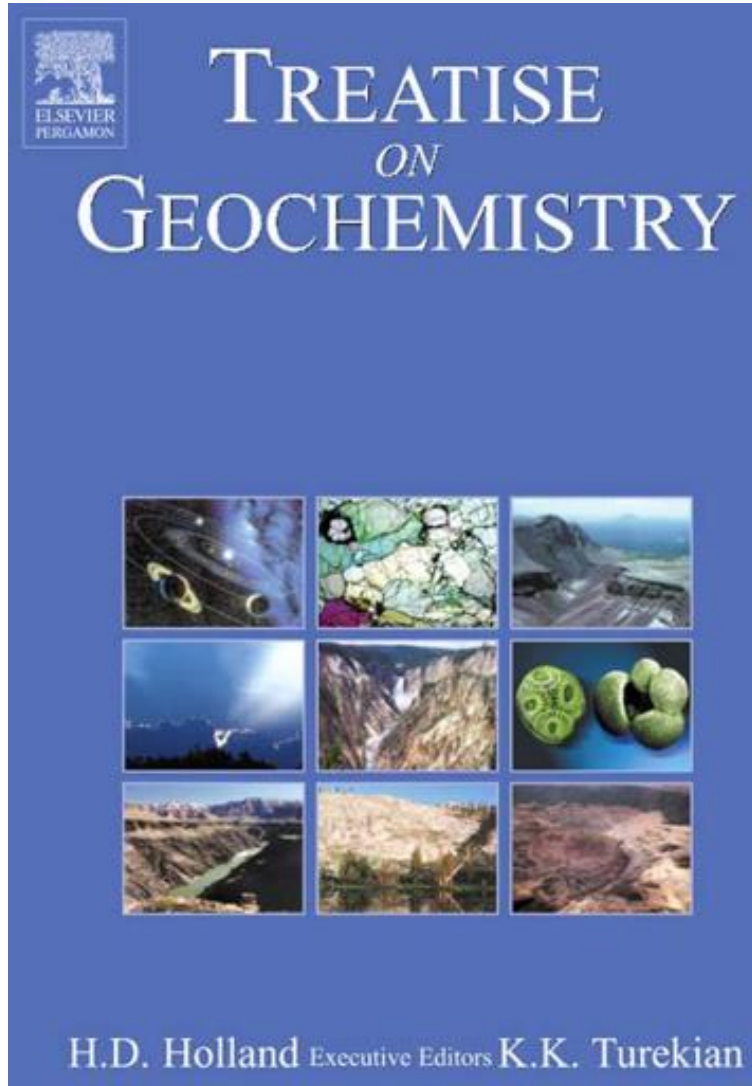
The first Wiki deadline is 7.4.!

Lecture 9: Geochemistry, minerals

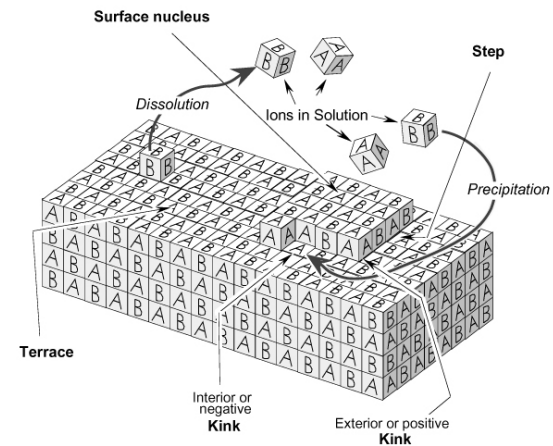
- Geochemistry
 - The origin and abundance of elements
 - Goldschmidt classification
 - Geophysical exploration
- Minerals
 - Systematic classification
 - Silicates
 - Aluminosilicates
 - Hardness as an example of a physical property



Literature



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 iron 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 (\dots) 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.

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

Main origin of chemical elements

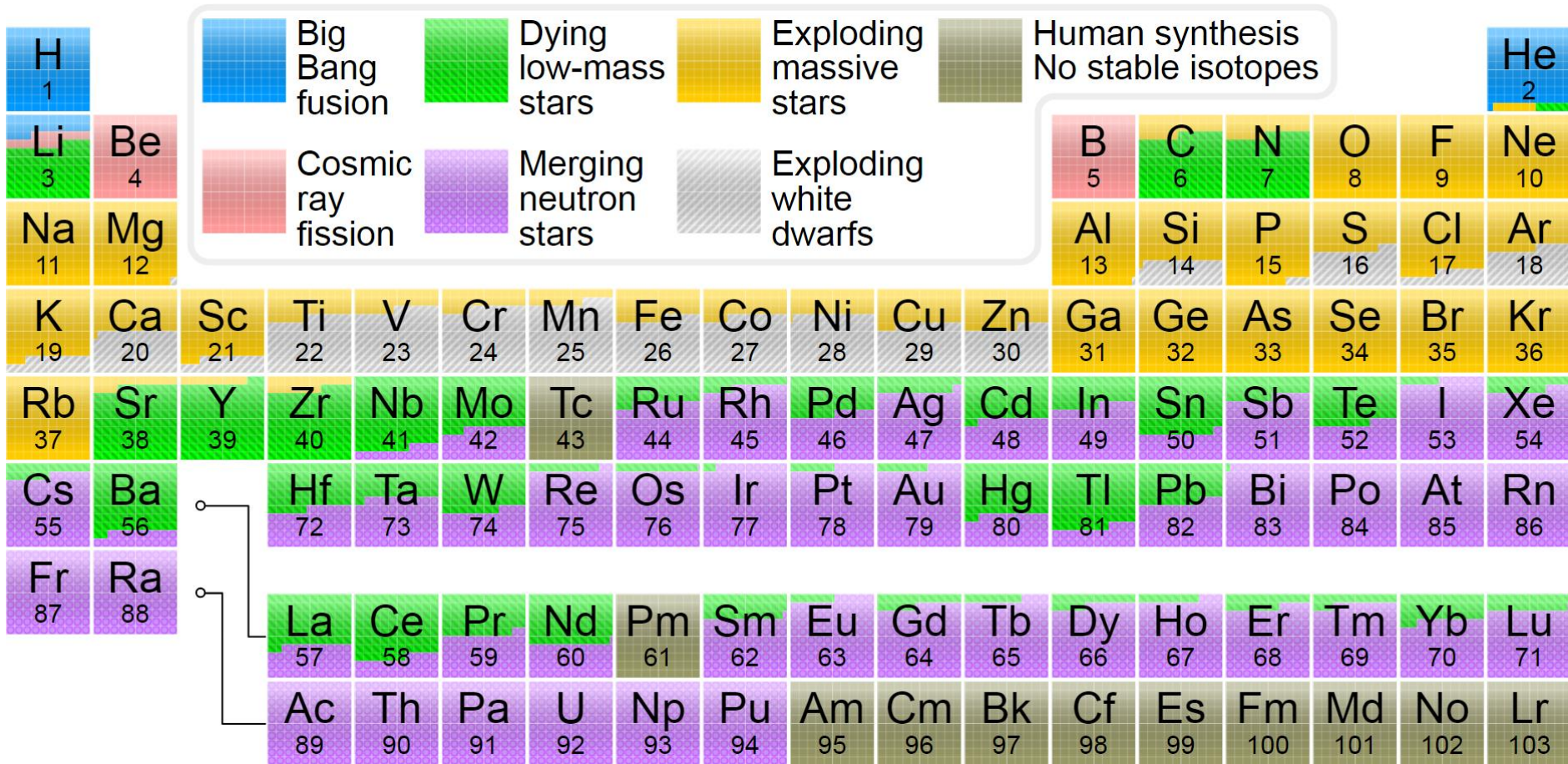


Figure: [Wikipedia](https://en.wikipedia.org/wiki/Stellar_nucleosynthesis)

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

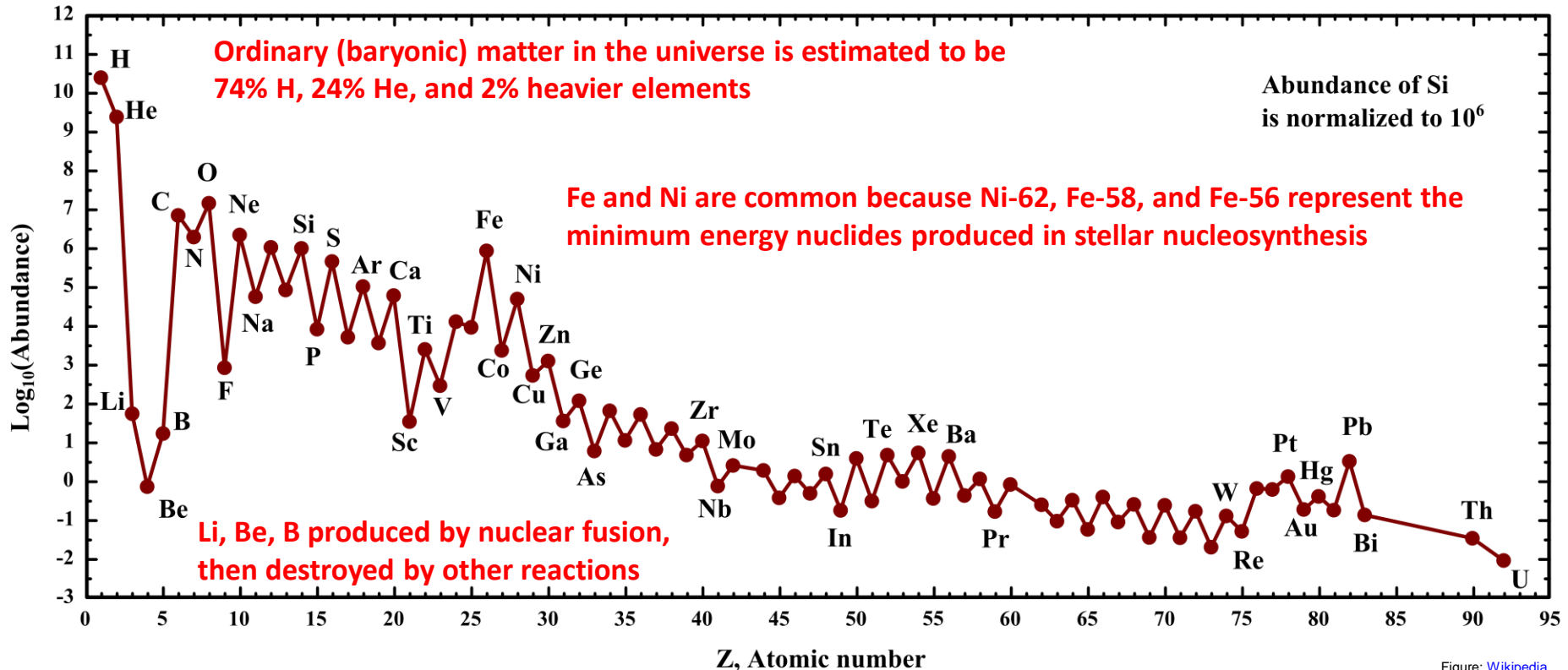


Figure: [Wikipedia](#)

Two general trends:

1. 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)
2. A decrease in abundance as elements become heavier

Abundances of the elements in the Earth's crust

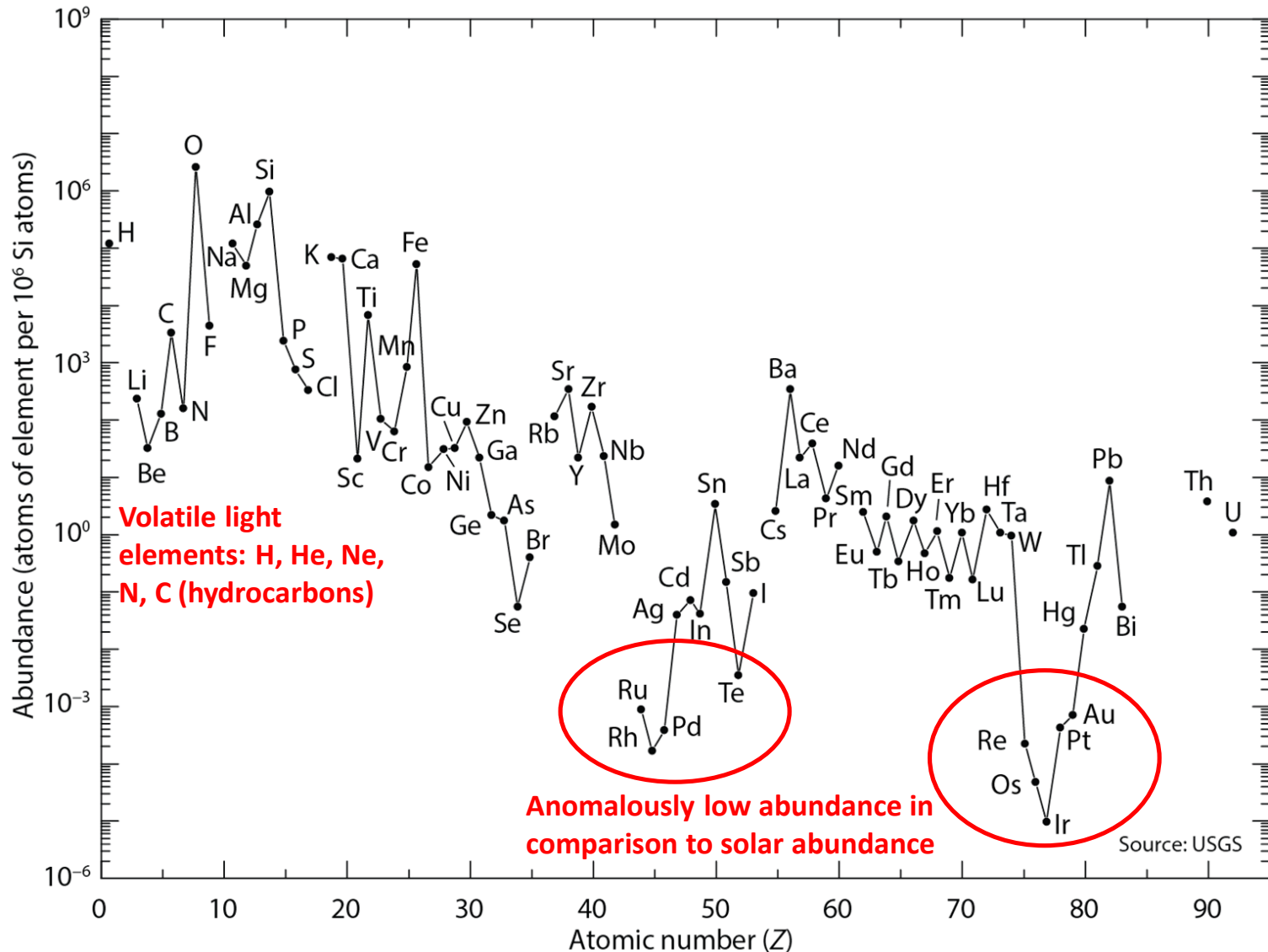


Figure: AJK

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

Shannon ionic radii:

 $O^{2-} = 140 \text{ pm}$ $Si^{4+} = 40 \text{ pm}$

<i>Order of abundance</i>	<i>Element</i>	<i>Weight % in crust</i>	<i>Molar % in crust</i>	<i>Volume % in crust</i>	<i>Typical natural form at Earth surface</i>
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".

Goldschmidt classification (1)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Group →																		
↓ Period																		
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	*	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	**	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	71 Lu	
		**	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	103 Lr	

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

Goldschmidt classification:

Lithophile	Siderophile	Chalcophile	Atmophile	Synthetic
------------	-------------	-------------	-----------	-----------

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

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, CO₂, hydrocarbons

Structure of Earth

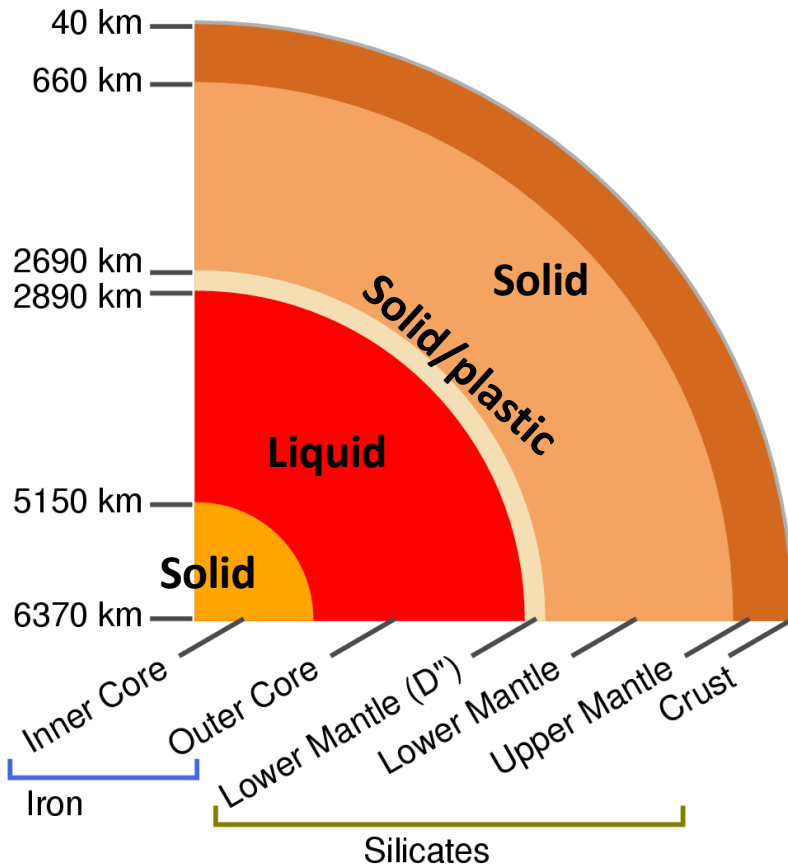


Figure: <http://backreaction.blogspot.fi/2010/06/diamonds-in-earth-science.html>

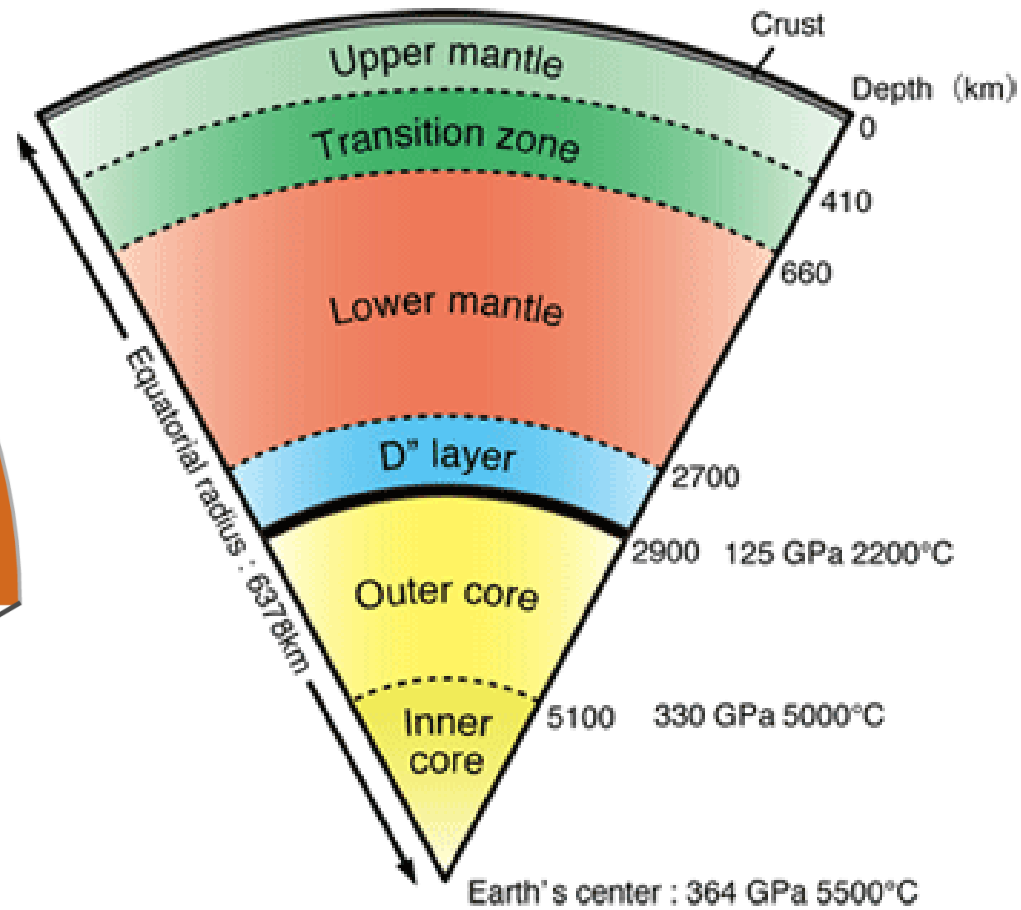


Figure: http://www.spring8.or.jp/en/news_publications/research_highlights/no_57/

Example: graphite-diamond phase transition occurs at ~130 km depth for $T = 800^{\circ}\text{C}$

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



Accessibility and supply of elements (1)

1 H 1.00794																2 He 4.002602	
3 Li 6.941	4 Be 9.012182																
11 Na 22.98977	12 Mg 24.3050																
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

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

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
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)

Actinides ‡

Accessibility and supply of elements (2)

- 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, supply Rare Earth Elements are often discussed as critical in supply
 - For REE, it is actually a question of supply and demand
 - Currently, China is producing them cheaply enough
 - If the price increases, known locations can be opened in US, Canada, ...
- So far, new supply of elements has always emerged when the price has been right
- The key question is, should we really push to find more elements at any cost?
 - Environmental problems become more severe as previously inaccessible resources are being utilized
 - Minerals are one of the most important reasons to human conflicts (e.g. Democratic Republic of the Congo)
 - It's foolish 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 CRMs with new functional materials
 - All these tasks require **chemists** and **materials scientists**!

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 5400 minerals (2019)



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⁻)																																													
<p style="text-align: center; background-color: #ffe6e6;">Native elements</p> <p style="text-align: center;">Sulfur (S) Diamond (C) Copper (Cu)</p>	<p style="text-align: center; background-color: #ffe6e6;">Fluorides</p> <p style="text-align: center;">Fluorite (CaF₂)</p> <hr/> <p style="text-align: center;">Halides ("Group VII -ides") (and thus minerals with 1- anions)</p> <p style="text-align: center; background-color: #ffe6e6;">Chlorides</p> <p style="text-align: center;">Halite (NaCl)</p> <hr/> <p style="text-align: center; background-color: #ffe6e6;">Bromides</p> <p style="text-align: center;">Bromargyrite (AgBr)</p> <hr/> <p style="text-align: center; background-color: #ffe6e6;">Iodides</p> <p style="text-align: center;">Iodargyrite (AgI)</p>	<p>Fluosalts: Fluoborates Ferrucite (NaBF₄) Fluosilicates Hieratite (K₂SiF₆)</p>	<p style="writing-mode: vertical-rl; transform: rotate(180deg);">Negative charge in mineral comes from halide anions</p>																																												
	<p style="text-align: center; background-color: #ffe6e6;">Oxides</p> <p style="text-align: center;">Hematite (Fe₂O₃)</p>	<p style="text-align: center; background-color: #ffe6e6;">Oxysalts:</p> <p style="text-align: center; background-color: #ffe6e6;">Silicates</p> <p style="text-align: center;">Vanadates Arsenates Sulfites Borates Chromates Selenates Arsenites Carbonates Niobates Antimonates Selenites Nitrates Molybdates Tellurates Antimonites Phosphates Tantalates Iodates Tellurites Sulfates Tungstates Calcite (CaCO₃)</p>		<p style="writing-mode: vertical-rl; transform: rotate(180deg);">Negative charge in mineral comes from anions of Group VI elements. For more, see "Radical groups in minerals . . .".</p>																																											
	<p style="text-align: center;">"Group VI -ides" (and thus minerals with 2- anions)</p> <p style="text-align: center; background-color: #ffe6e6;">Sulfides</p> <p style="text-align: center;">Galena (PbS)</p>	<p>Sulfosalts: Sulfarsenates Sulfovanadates Sulfogermanates Sulfarsenites Sulfantimonates Sulfantimonites Pyrrargyrite (Ag₃SbS₃) Sulfostannates Sulfobismuthites</p>																																													
	<p style="text-align: center; background-color: #ffe6e6;">Selenides</p> <p style="text-align: center;">Achavalite (FeSe)</p>	<p>Seleniosalts: Selenioantimonates Permingeatite (Cu₃SbSe₄) Seleniobismuthites</p>																																													
	<p style="text-align: center; background-color: #ffe6e6;">Tellurides</p> <p style="text-align: center;">Altaite (PbTe)</p>	<p>Telluriosalts: Telluribismuthites Volynskite (AgBiTe₂)</p>																																													
	<p style="text-align: center;">"Group V -ides" (and thus minerals with 3- anions)</p> <p style="text-align: center; background-color: #ffe6e6;">Nitrides</p> <p style="text-align: center;">Osbornite (TiN)</p> <p style="text-align: center; background-color: #ffe6e6;">Phosphides</p> <p style="text-align: center;">Barringerite (Fe,Ni)₂P</p> <p style="text-align: center; background-color: #ffe6e6;">Arsenides</p> <p style="text-align: center;">Löllingite (FeAs₂)</p> <p style="text-align: center; background-color: #ffe6e6;">Antimonides & Bismuthides</p> <p style="text-align: center;">Sobolevskite (PdBi)</p>	<div style="border: 1px solid black; padding: 5px; margin: 10px auto; width: fit-content;"> <p>Groups containing relatively abundant minerals are highlighted; examples of minerals for various groups are in gray.</p> </div>			<div style="border: 1px solid black; padding: 5px; margin: 10px auto; width: fit-content;"> <p>A bit of the periodic table:</p> <table style="border-collapse: collapse; text-align: center; margin: 0 auto;"> <tr> <td></td><td></td><td></td><td></td><td></td><td style="text-align: right;">VIII</td> </tr> <tr> <td></td><td>IV</td><td>V</td><td>VI</td><td>VII</td><td>He</td> </tr> <tr> <td>B</td><td>C</td><td>N</td><td>O</td><td>F</td><td>Ne</td> </tr> <tr> <td>Al</td><td>Si</td><td>P</td><td>S</td><td>Cl</td><td>Ar</td> </tr> <tr> <td></td><td>Ge</td><td>As</td><td>Se</td><td>Br</td><td>Kr</td> </tr> <tr> <td></td><td>Sn</td><td>Sb</td><td>Te</td><td>I</td><td>Xe</td> </tr> <tr> <td></td><td>Pb</td><td>Bi</td><td>Po</td><td>At</td><td>Ra</td> </tr> </table> </div>						VIII		IV	V	VI	VII	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
									VIII																																						
	IV	V	VI		VII	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																																										
<p style="text-align: center;">"Group IV -ides" (and thus minerals with 4- anions)</p> <p style="text-align: center; background-color: #ffe6e6;">Carbides</p> <p style="text-align: center;">Moissanite (SiC)</p> <p style="text-align: center; background-color: #ffe6e6;">Silicides</p> <p style="text-align: center;">Gupeite (Fe₃Si)</p>		<p style="writing-mode: vertical-rl; transform: rotate(180deg);">Negative charge in mineral comes from anions of Group IV and V elements</p>																																													

This table does not show hybrid categories that would include minerals like breunite (Ca₂CO₃F₂) or kermesite (Sb₂S₂O). It also does not show H⁺-bearing minerals; their inclusion would best be shown with a third dimension leading to hydroxides, bicarbonates, bisulfates, etc.

A table of systematic mineralogy II: redox implications

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-})																										
<p>Native elements</p> <p>Sulfur (S) Diamond (C) Copper (Cu)</p> <p>Formation of these minerals typically requires intermediate or reducing redox conditions, because all elements that form native minerals also have charged valence states, commonly oxidized states, that they might otherwise take.</p>	<p>Fluorides Fluorite (CaF_2)</p> <hr/> <p>Halides ("Group VII -ides") (and thus minerals with 1- anions)</p> <p>Chlorides Halite (NaCl)</p> <p>Bromides Bromargyrite (AgBr)</p> <p>Iodides Iodargyrite (AgI)</p>	<p>Fluosalts: Fluoborates Ferrucite (NaBF_4) Fluosilicates Hieratite (K_2SiF_6)</p> <hr/> <p>Formation of the halide minerals is indifferent to redox conditions, because the Group VII elements involved have one, or essentially only one, valence state (-1). ("Essentially only one" is required because iodine <i>can</i> also form iodate minerals).</p>	Negative charge in mineral comes from halide anions																									
	<p>Oxides Hematite (Fe_2O_3)</p> <p style="color: red;">Formation of these minerals requires at least somewhat oxidizing conditions, because elements involved (e.g., C, N, P, S) have more reduced valence states as alternatives. These minerals thus commonly form in near-Earth-surface environments.</p>	<p>Oxysalts:</p> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="border: 1px solid black;">Silicates</td> <td style="border: 1px solid black;">Vanadates</td> <td style="border: 1px solid black;">Arsenates</td> <td style="border: 1px solid black;">Sulfites</td> </tr> <tr> <td style="border: 1px solid black;">Borates</td> <td style="border: 1px solid black;">Chromates</td> <td style="border: 1px solid black;">Selenates</td> <td style="border: 1px solid black;">Arsenites</td> </tr> <tr> <td style="border: 1px solid black;">Carbonates</td> <td style="border: 1px solid black;">Niobates</td> <td style="border: 1px solid black;">Antimonates</td> <td style="border: 1px solid black;">Selenites</td> </tr> <tr> <td style="border: 1px solid black;">Nitrates</td> <td style="border: 1px solid black;">Molybdates</td> <td style="border: 1px solid black;">Tellurates</td> <td style="border: 1px solid black;">Antimonites</td> </tr> <tr> <td style="border: 1px solid black;">Phosphates</td> <td style="border: 1px solid black;">Tantalates</td> <td style="border: 1px solid black;">Iodates</td> <td style="border: 1px solid black;">Tellurites</td> </tr> <tr> <td style="border: 1px solid black;">Sulfates</td> <td style="border: 1px solid black;">Tungstates</td> <td style="border: 1px solid black;">Calcite (CaCO_3)</td> <td></td> </tr> </table>	Silicates	Vanadates	Arsenates	Sulfites	Borates	Chromates	Selenates	Arsenites	Carbonates	Niobates	Antimonates	Selenites	Nitrates	Molybdates	Tellurates	Antimonites	Phosphates	Tantalates	Iodates	Tellurites	Sulfates	Tungstates	Calcite (CaCO_3)		<p>Intermediate redox states</p> <p>Sulfarsenates Sulfovanadates Sulfogermanates Sulfarsenites Sulfantimonates Sulfantimonites Sulfostannates Sulfobismuthites</p> <p>Pyrargyrite (Ag_3SbS_3)</p>	Negative charge in mineral comes from anions of Group VI elements
	Silicates	Vanadates	Arsenates	Sulfites																								
	Borates	Chromates	Selenates	Arsenites																								
	Carbonates	Niobates	Antimonates	Selenites																								
	Nitrates	Molybdates	Tellurates	Antimonites																								
	Phosphates	Tantalates	Iodates	Tellurites																								
	Sulfates	Tungstates	Calcite (CaCO_3)																									
	<p>"Group VI -ides" (and thus minerals with 2- anions)</p> <p>Sulfides Galena (PbS)</p> <hr/> <p>Selenides Achavalite (FeSe)</p> <hr/> <p>Tellurides Altaite (PbTe)</p>	<p>Sulfosalts:</p> <p>Seleniosalts: Selenioantimonates Seleniobismuthites</p> <p>Telluriosalts: Telluribismuthites</p>	<p>Permingeatite (Cu_3SbSe_4)</p> <p>Volynskite (AgBiTe_2)</p>	Negative charge in mineral comes from anions of Group VI elements																								
	<p>"Group V -ides" (and thus minerals with 3- anions)</p> <p>Nitrides Osbornite (TiN)</p> <p>Phosphides Barringerite ($\text{Fe,Ni}_2\text{P}$)</p> <p>Arsenides Löllingite (FeAs_2)</p> <p>Antimonides & Bismuthides Sobolevskite (PdBi)</p>	<p>Formation of these minerals requires reducing conditions, because elements involved (e.g., C, N, P, S, As, Se, Sb) have more oxidized valence states as alternatives. For example, most nitride, phosphide, carbide, silicide, etc. minerals are known largely or only from meteorites, cosmic dust, or deep-earth samples. Likewise, many sulfides and sulfosalts are known from ore deposits that formed at depth rather than at the Earth's surface.</p>		Negative charge in mineral comes from anions of Group IV and V elements																								
<p>"Group IV -ides" (and thus minerals with 4- anions)</p> <p>Carbides Moissanite (SiC)</p> <p>Silicides Guepéite (Fe_3Si)</p>			Negative charge in mineral comes from anions of Group IV and V elements																									

The characterizations above are only generalizations about entire classes of minerals. For example, siderite ($\text{Fe}^{2+}\text{CO}_3$) requires somewhat reducing conditions to form, whereas molysite ($\text{Fe}^{3+}\text{Cl}_3$) would likely form in oxidizing conditions.

A table of systematic mineralogy IV: numbers of minerals

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-})		
<p style="text-align: center;">Native elements</p> <p style="text-align: center;">Sulfur (S) Diamond (C) Copper (Cu)</p> <p style="text-align: center; font-size: 1.2em;">(90)</p> <p>Only 31 elements occur as native minerals. The number above includes polymorphs (e.g., diamond, graphite, chaoite, and lonsdaleite) and naturally occurring alloys.</p>	<p style="text-align: center;">Fluorides Fluorite (CaF_2) (32)</p> <p style="text-align: center;">Halides ("Group VII -ides") (and thus minerals with 1- anions)</p> <p style="text-align: center;">Chlorides Halite (NaCl) (75)</p> <p style="text-align: center;">Bromides Bromargyrite (AgBr) (4)</p> <p style="text-align: center;">Iodides Iodargyrite (Agl) (3)</p>	<p>Fluosalts: (6) Fluoborates Ferruccite (NaBF_4) Fluosilicates Hieratite (K_2SiF_6)</p>	Negative charge in mineral comes from halide anions	
	<p style="text-align: center;">Oxides Hematite (Fe_2O_3)</p> <p style="text-align: center; font-size: 1.2em;">(255)</p>	<p>Oxysalts: (2700)</p>	<p>Silicates Vanadates Arsenates Sulfites Borates Chromates Selenates Arsenites Carbonates Niobates Antimonates Selenites Nitrates Molybdates Tellurates Antimonites Phosphates Tantalates Iodates Tellurites Sulfates Tungstates Calcite (CaCO_3)</p>	Negative charge in mineral comes from anions of Group VI elements
	<p style="text-align: center;">"Group VI -ides" (and thus minerals with 2- anions)</p> <p style="text-align: center;">Sulfides Galena (PbS)</p> <p style="text-align: center; font-size: 1.2em;">(138)</p>	<p>Sulfosalts: (250)</p>	<p>Sulfarsenates Sulfovanadates Sulfogermanates Sulfarsenites Sulfantimonates Sulfantimonites Pyrrargyrite (Ag_3SbS_3) Sulfostannates Sulfobismuthites</p>	
	<p style="text-align: center;">Selenides Achalite (FeSe) (37)</p>	<p>Seleniosalts: (2)</p>	<p>Selenioantimonates Permingeaitite (Cu_3SbSe_4) Seleniobismuthites</p>	
	<p style="text-align: center;">Tellurides Altaite (PbTe) (34)</p>	<p>Tellurisalts: (1)</p>	<p>Telluribismuthites Volynskite (AgBiTe_2)</p>	
	<p style="text-align: center;">"Group V -ides" (and thus minerals with 3- anions)</p> <p style="text-align: center;">Nitrides Osbornite (TiN) (4)</p> <p style="text-align: center;">Phosphides Barringerite (Fe,Ni)₂P (3)</p> <p style="text-align: center;">Arsenides Löllingite (FeAs_2) (21)</p> <p style="text-align: center;">Antimonides & Bismuthides Sobolevskite (PdBi) (6)</p>	<div style="border: 1px solid black; padding: 5px; display: inline-block;"> <p style="text-align: center; font-size: 1.5em;">(37)</p> <p style="font-size: 0.8em;">Number of minerals known in each category The number shown for oxides does not include minerals that are solely hydroxides.</p> </div>		
	<p style="text-align: center;">"Group IV -ides" (and thus minerals with 4- anions)</p> <p style="text-align: center;">Carbides Moissanite (SiC) (5)</p> <p style="text-align: center;">Silicides Gupeite (Fe_3Si) (4)</p>	<p>The numbers shown here can be taken at face value as an indication that there are more oxysalt and oxide minerals than any other kinds. That would not be surprising, given that oxygen is the most abundant element in Earth's crust. Alternately, the numbers shown here can be taken to reflect the greatest human access to oxidizing environments at Earth's surface, and our inability to sample the reducing environments in Earth's deep interior to any significant extent.</p>		

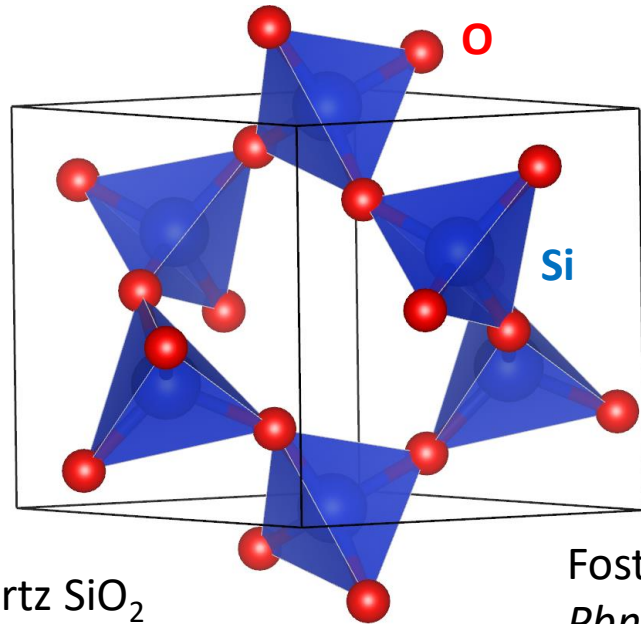
Room for update!

As of 2004, a total of about 4100 minerals had been formally recognized by the International Mineralogical Association. For the list, see Mandarin, J.A., and Back, M.E., 2004, Fleischer's Glossary of Mineral Names: Tuscon, The Mineralogical Record Inc., 309 p.

LBR SystematicMinTable10_11/2007

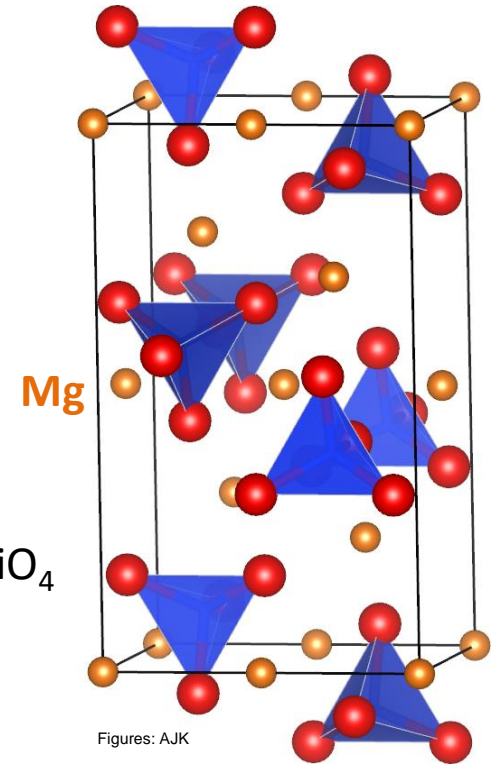
Some Fundamentals of Mineralogy and Geochemistry, L. Bruce Railsback, <http://www.gly.uga.edu/railsback/FundamentalsIndex.html>

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

Si:O ratio	Number of oxygens per Si		Type of silicate anion	Examples
	Bridging	Non-bridging		
1:4	0	4	Isolated SiO_4^{4-}	Mg_2SiO_4 olivine, Li_4SiO_4
1:3.5	1	3	Dimer $\text{Si}_2\text{O}_7^{6-}$	$\text{Ca}_3\text{Si}_2\text{O}_7$ rankinite, $\text{Sc}_2\text{Si}_2\text{O}_7$ thortveite
1:3	2	2	Chains $(\text{SiO}_3)_n^{2n-}$ Rings, e.g. $\text{Si}_3\text{O}_9^{6-}$ $\text{Si}_6\text{O}_{18}^{12-}$	Na_2SiO_3 , MgSiO_3 pyroxene CaSiO_3^a , $\text{BaTiSi}_3\text{O}_9$ benitoite Beryl
1:2.5	3	1	Sheets $(\text{Si}_2\text{O}_5)_n^{2n-}$	$\text{Na}_2\text{Si}_2\text{O}_5$
1:2	4	0	3D framework	SiO_2^b

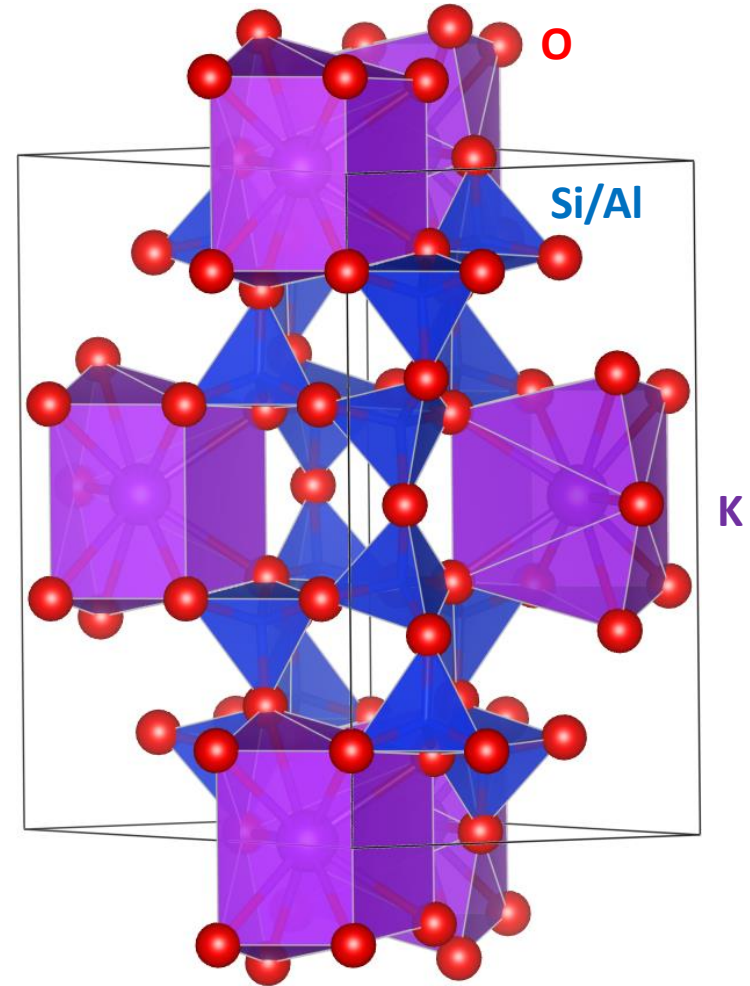
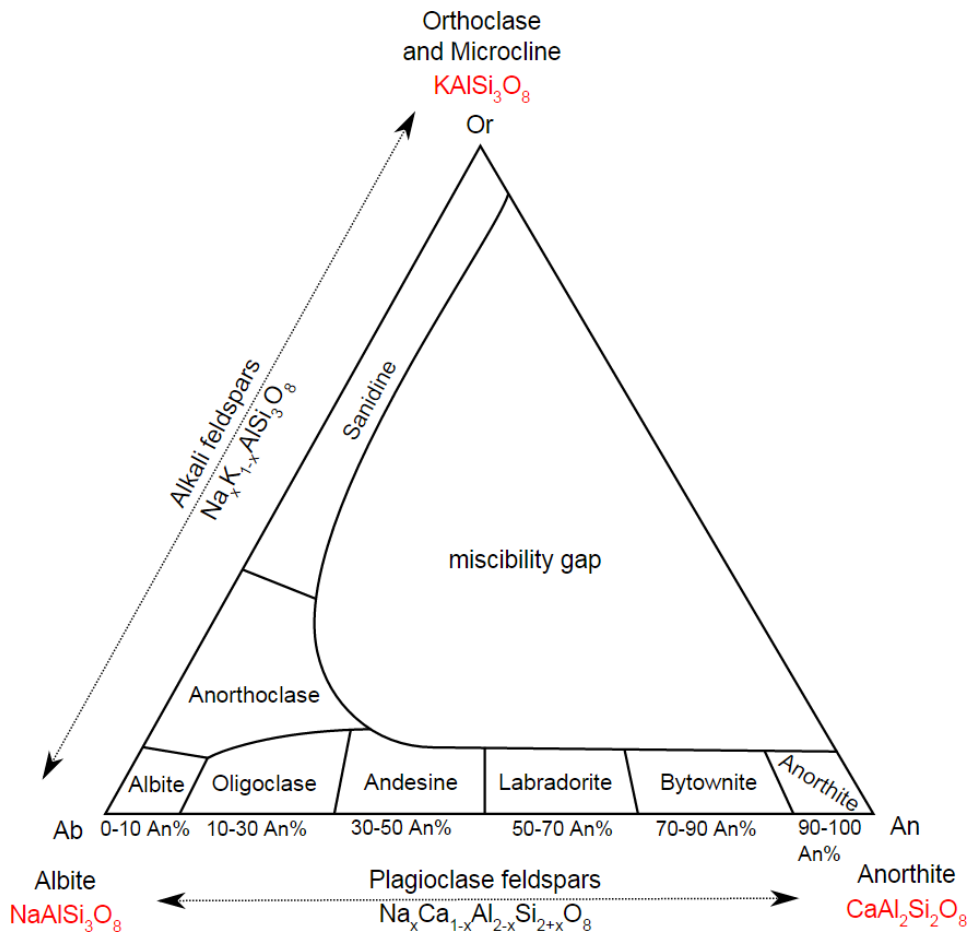
"Tectosilicates", Quartz family + aluminosilicates: 75% of the crust

^a CaSiO_3 is dimorphic. One polymorph has $\text{Si}_3\text{O}_9^{6-}$ rings and the other has infinite $(\text{SiO}_3)_n^{2n-}$ chains.

^bThe 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



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

Figure: AJK

Figure: Wikipedia

Aluminosilicates: Zeolites

- Microporous aluminosilicate minerals
 - Cronstedt 1756: heating *stilbite*, $\text{NaCa}_4(\text{Si}_{27}\text{Al}_9)\text{O}_{72}\cdot 28(\text{H}_2\text{O})$, produced steam
 - *Zéō* -> to boil
 - *Líthos* -> rock
- Can be considered as molecular sieves, with actual industrial applications in:
 - Ion-exchange (e.g. water purification and softening)
 - Catalysis (e.g. In petrochemical industry)
- <http://www.iza-structure.org/databases/>
- <http://www.hypotheticalzeolites.net/>

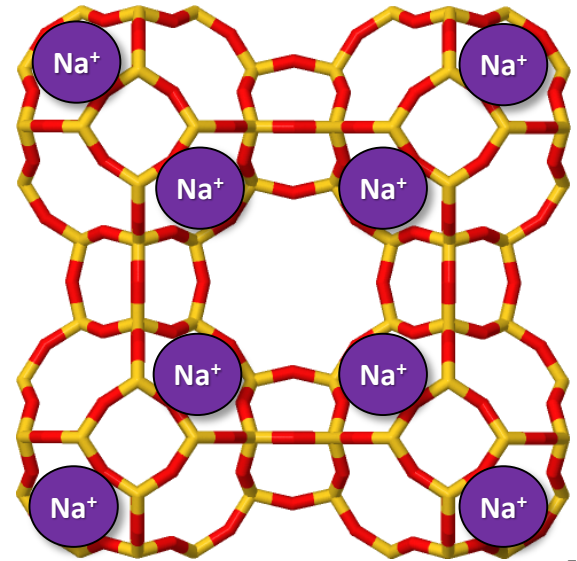
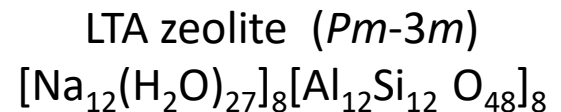
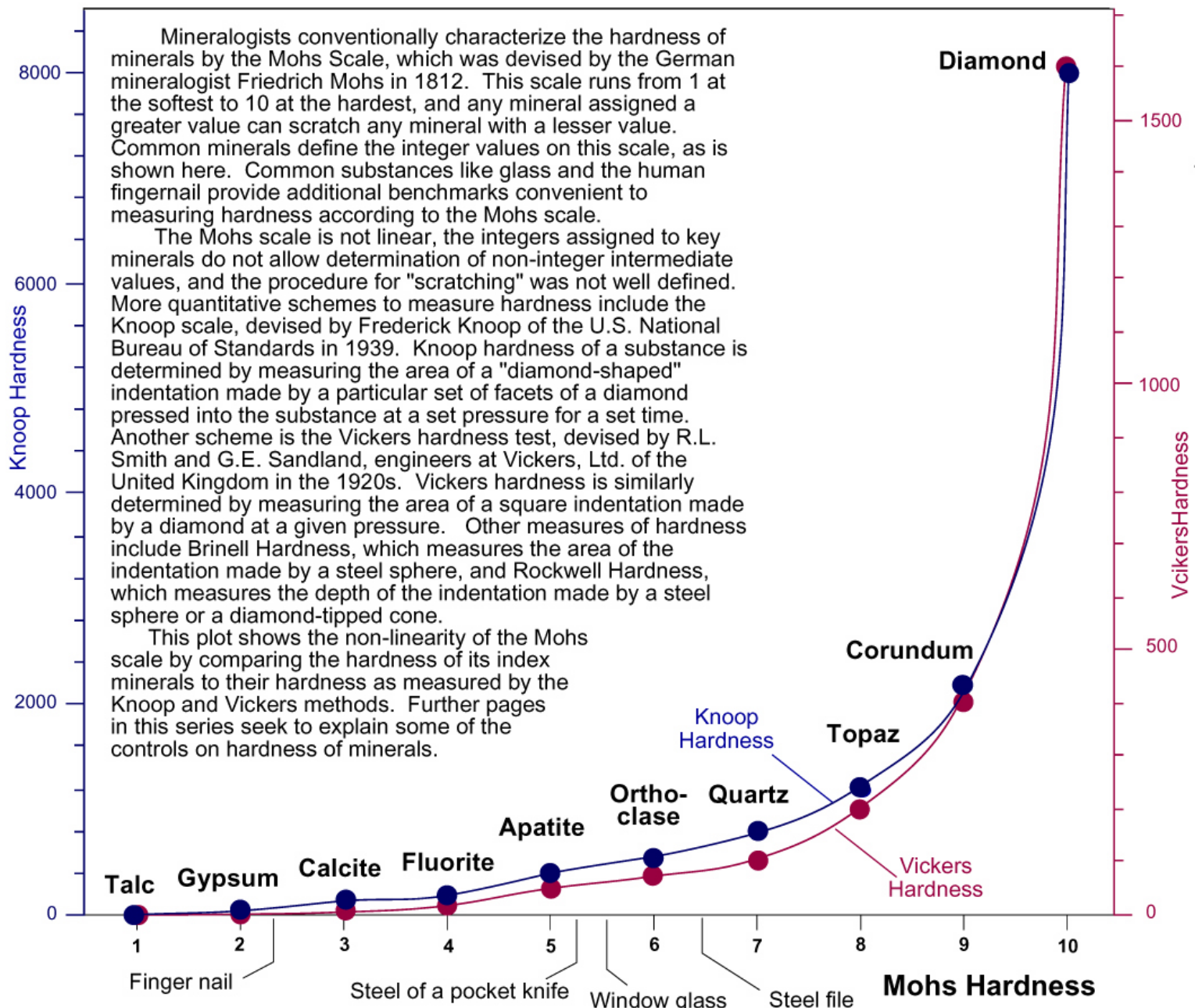


Figure: AJK

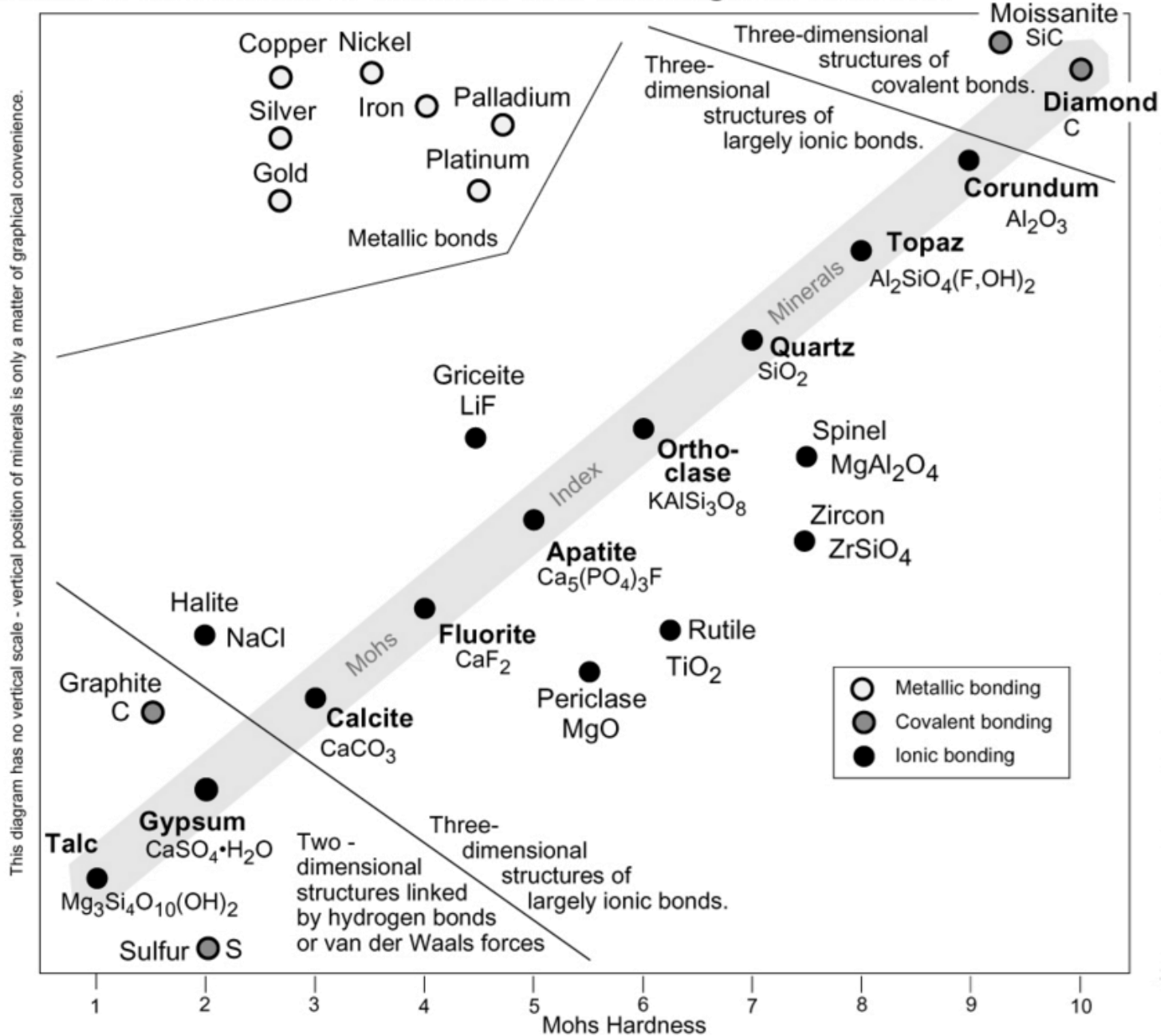


Extra slides:
Hardness of minerals

Hardness of minerals I: the Mohs scale

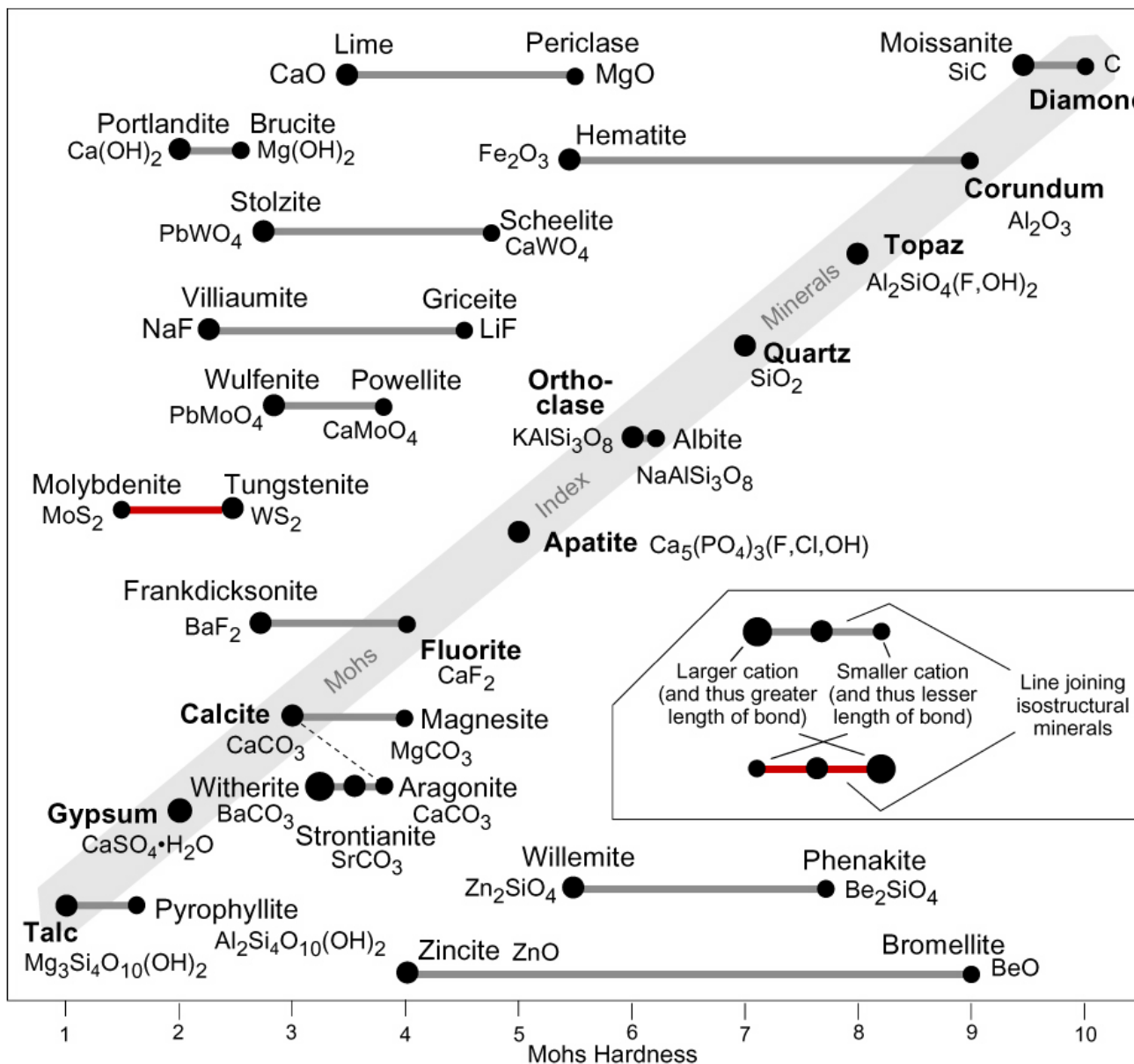


Hardness of minerals II: variation with bonding and structure



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

This diagram has no vertical scale - vertical position of minerals is only a matter of graphical convenience.



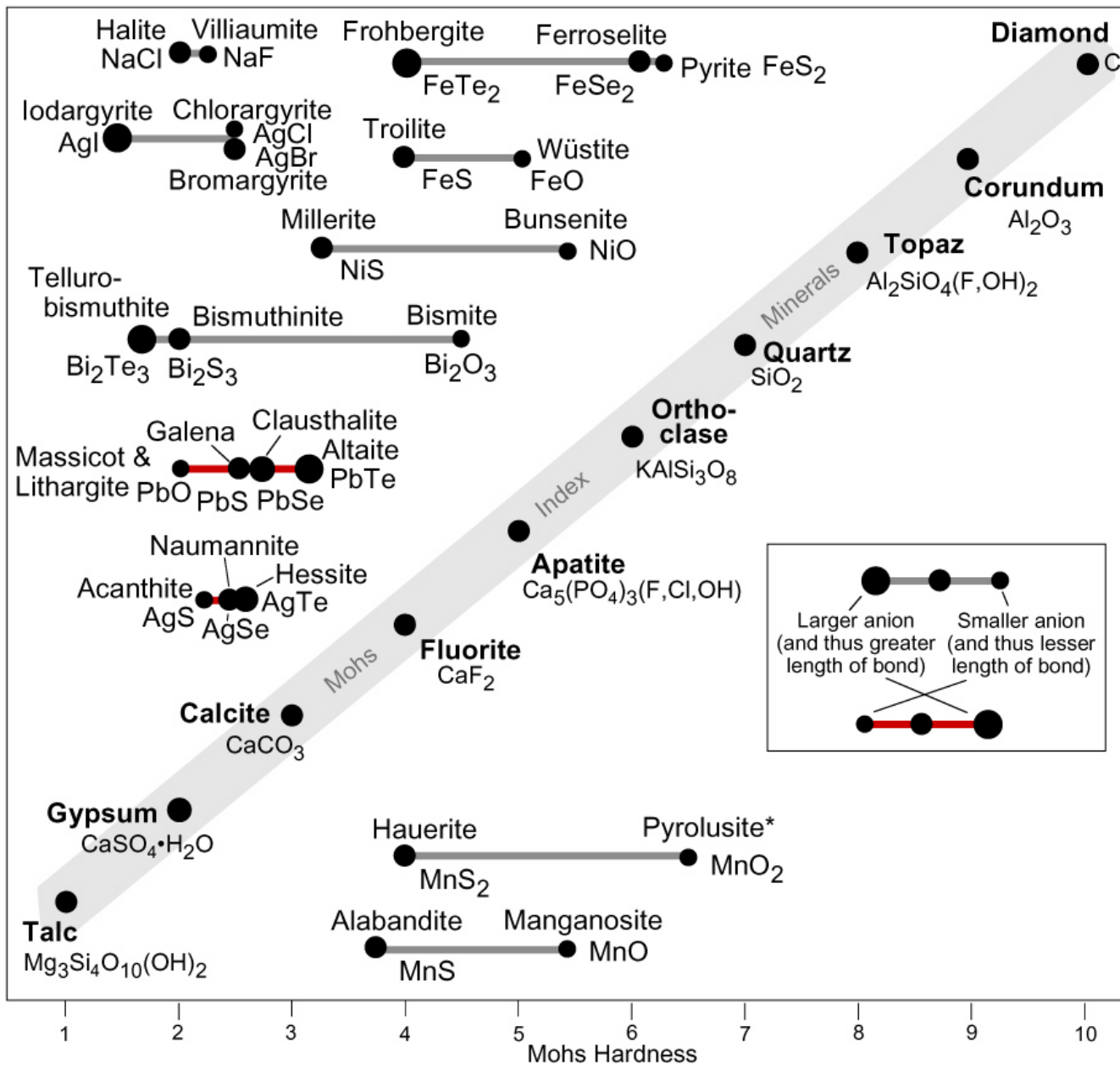
One control on hardness of a mineral is the length of bonds within that mineral. To illustrate this point, this diagram shows pairs or sets of isostructural minerals. In almost all of the examples shown on this diagram, minerals with larger cations, and thus greater bond lengths, are softer than their 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.

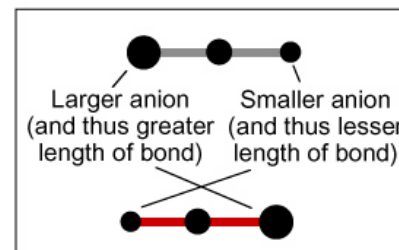
Hardness of minerals IVb: variation with bond length and anion size

This diagram has no vertical scale - vertical position of minerals is only a matter of graphical convenience.



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.

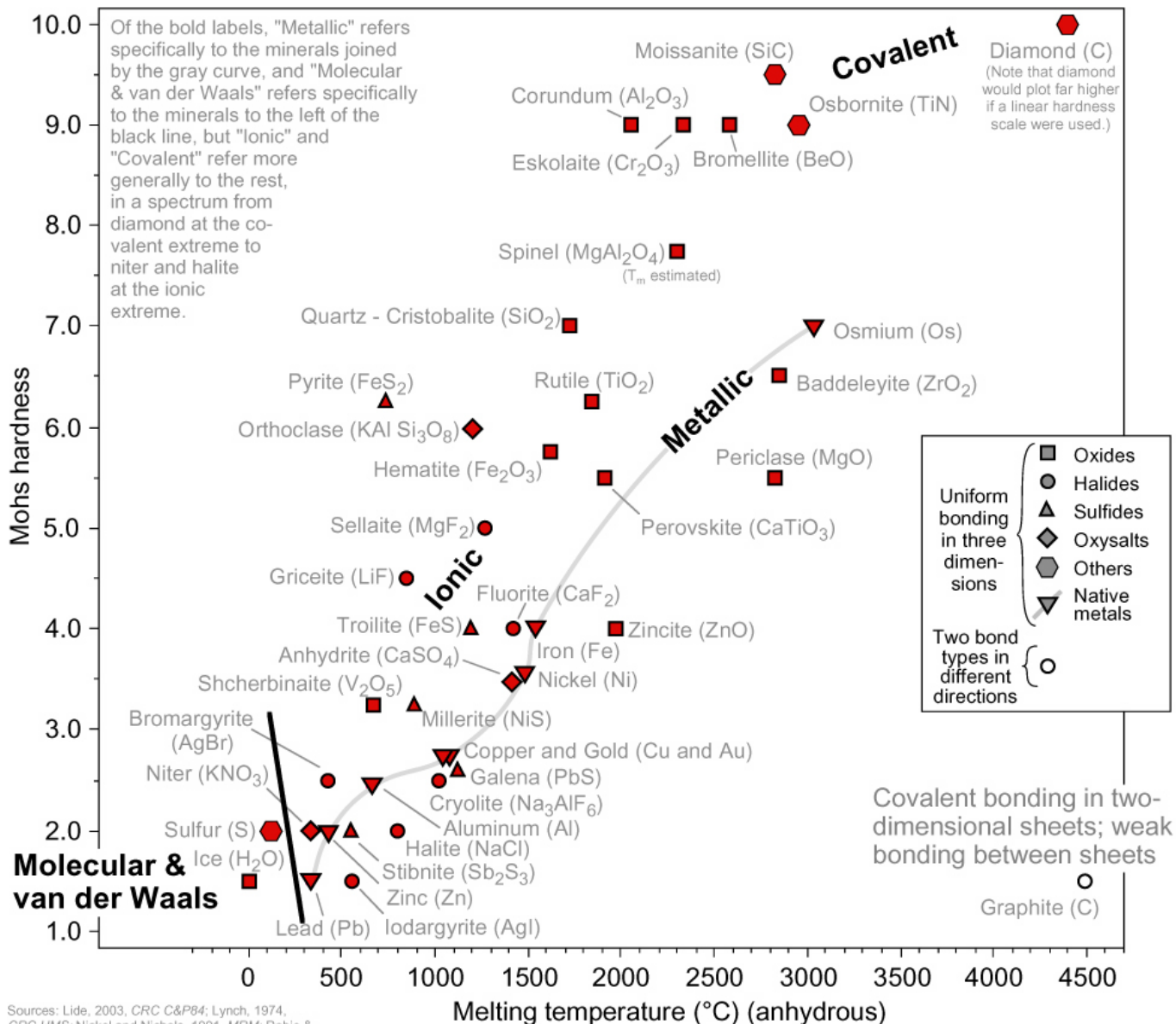
However, in two cases shown here (the ones joined by red lines), larger anions lead to harder minerals. These are the examples where soft cations, Ag^+ and Pb^{2+} , bond to 2- anions. In these cases, the bonds of soft cations to increasingly large and thus increasingly soft anions may lead to sufficiently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



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.

Sources: Lide, 2003, CRC C&P84; Lynch, 1974, CRC HMS; Nickel and Nichols, 1991, MRM; Robie & Hemingway, 1995, USGS 2131; Strunz and Nickel, 2001, SMT.