5.03: Principles of Inorganic Chemistry I

Christopher C. Cummins, Stephen J. Lippard

Massachusetts Institute of Technology

Spring, 2015

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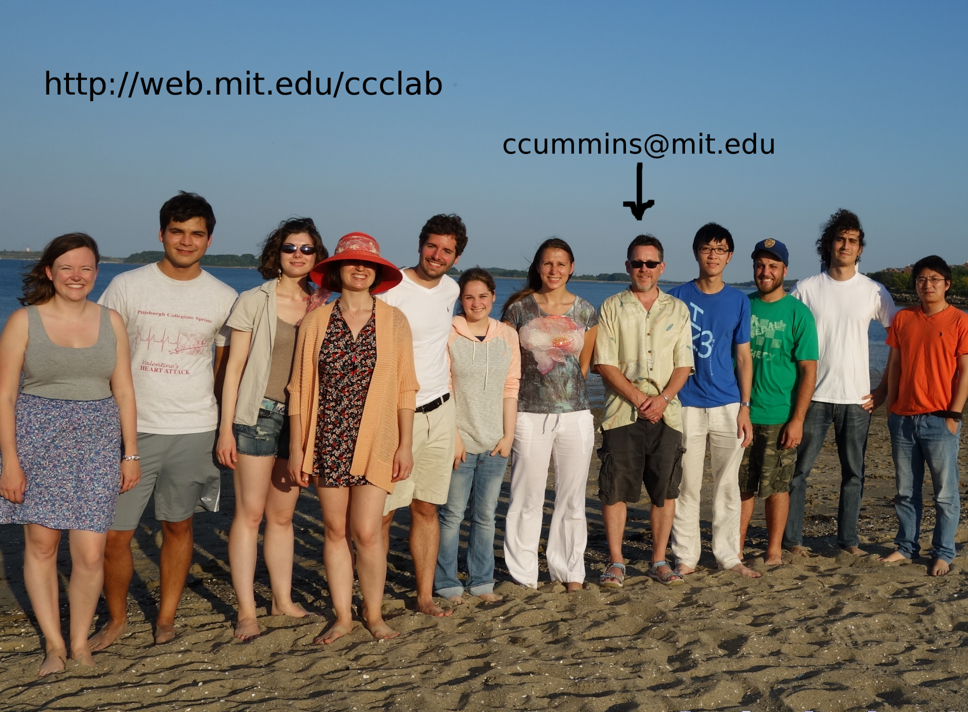
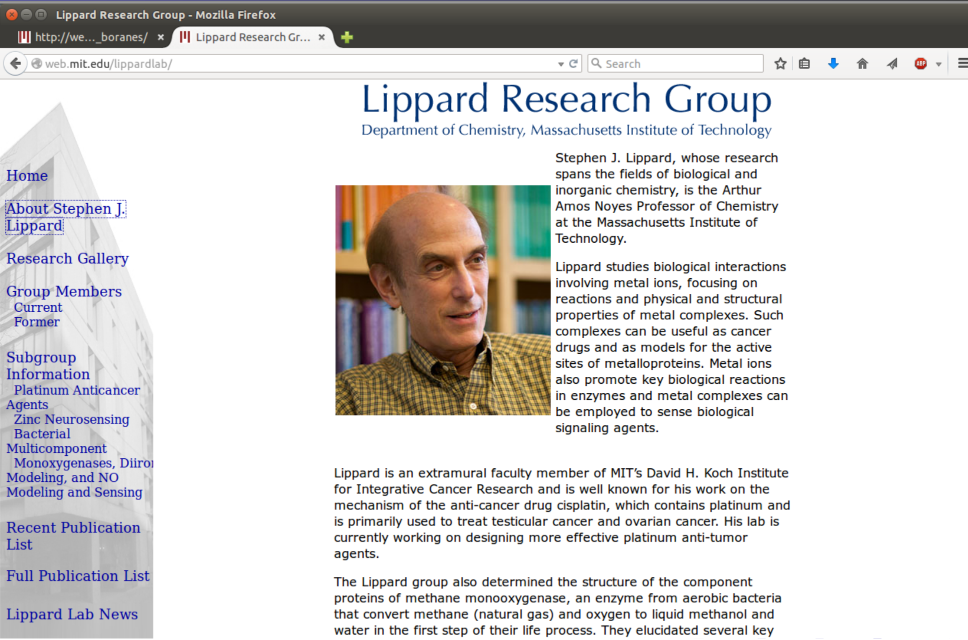


Professor Stephen J. Lippard, lippard@mit.edu



Lippard Research Group

Department of Chemistry, Massachusetts Institute of Technology

Home

About Stephen J. Lippard

Research Gallery

Group Members
- Current
- Former

Subgroup Information
- Platinum Anticancer Agents
- Zinc Neurosensing
- Bacterial Multicomponent Monoxygenases, Diiro Modeling, and NO Modeling and Sensing

Recent Publication List

Full Publication List

Lippard Lab News

Stephen J. Lippard, whose research spans the fields of biological and inorganic chemistry, is the Arthur Amos Noyes Professor of Chemistry at the Massachusetts Institute of Technology.

Lippard studies biological interactions involving metal ions, focusing on reactions and physical and structural properties of metal complexes. Such complexes can be useful as cancer drugs and as models for the active sites of metalloproteins. Metal ions also promote key biological reactions in enzymes and metal complexes can be employed to sense biological signaling agents.

Lippard is an extramural faculty member of MIT's David H. Koch Institute for Integrative Cancer Research and is well known for his work on the mechanism of the anti-cancer drug cisplatin, which contains platinum and is primarily used to treat testicular cancer and ovarian cancer. His lab is currently working on designing more effective platinum anti-tumor agents.

The Lippard group also determined the structure of the component proteins of methane monooxygenase, an enzyme from aerobic bacteria that convert methane (natural gas) and oxygen to liquid methanol and water in the first step of their life process. They elucidated several key

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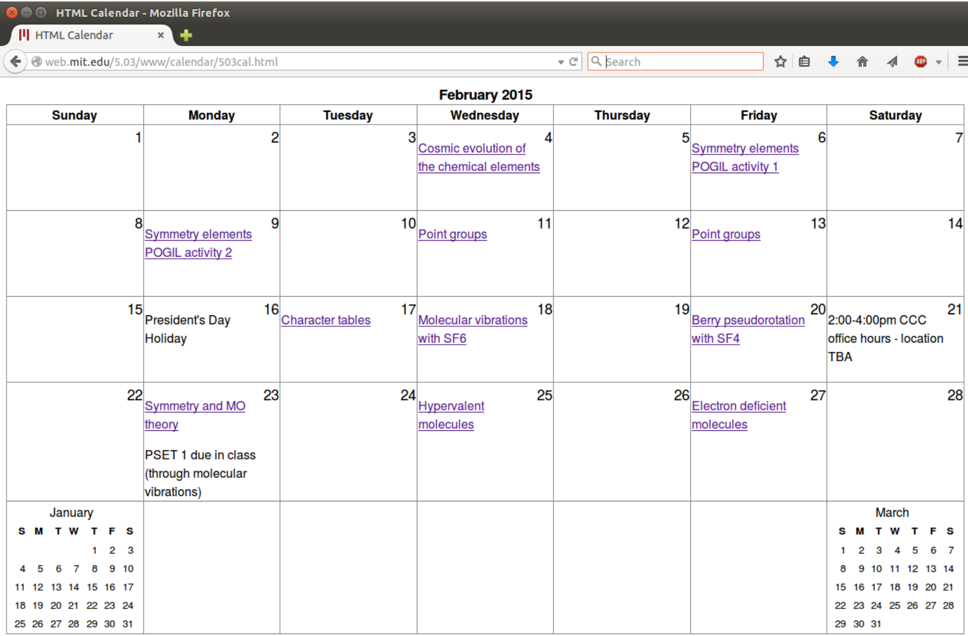
TA: Laura Avena, avena@mit.edu



February 2015

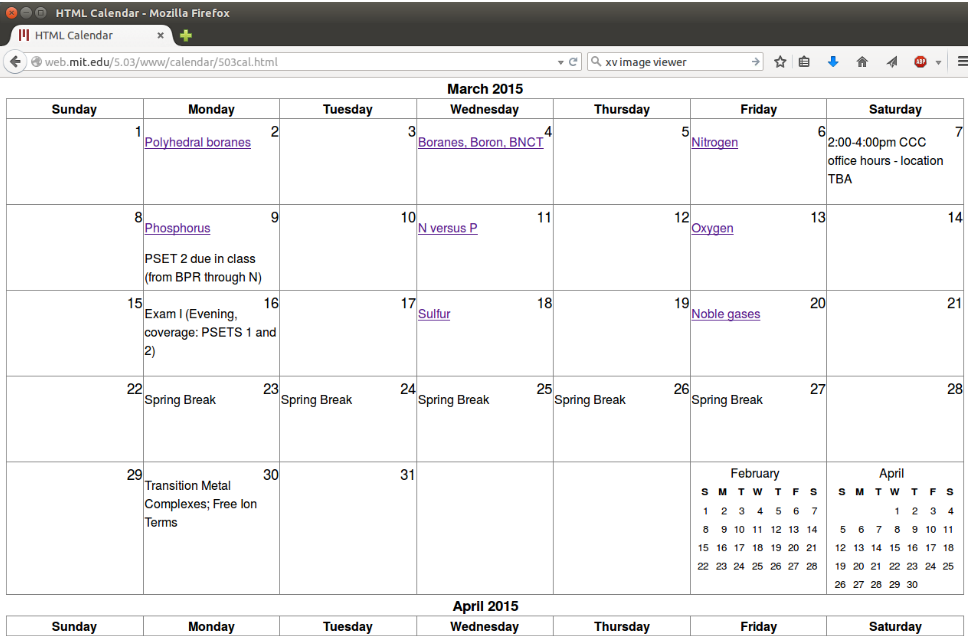
Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
1	2	3	4 Cosmic evolution of the chemical elements	5	6 Symmetry elements POGIL activity 1	7
8	9 Symmetry elements POGIL activity 2	10	11 Point groups	12	13 Point groups	14
15	16 President's Day Holiday	17 Character tables	18 Molecular vibrations with SF6	19	20 Berry pseudorotation with SF4	21 2:00-4:00pm CCC office hours - location TBA
22	23 Symmetry and MO theory PSET 1 due in class (through molecular vibrations)	24	25 Hypervalent molecules	26	27 Electron deficient molecules	28

January

S	M	T	W	T	F	S
				1	2	3
4	5	6	7	8	9	10
11	12	13	14	15	16	17
18	19	20	21	22	23	24
25	26	27	28	29	30	31

March

S	M	T	W	T	F	S
1	2	3	4	5	6	7
8	9	10	11	12	13	14
15	16	17	18	19	20	21
22	23	24	25	26	27	28
29	30	31				

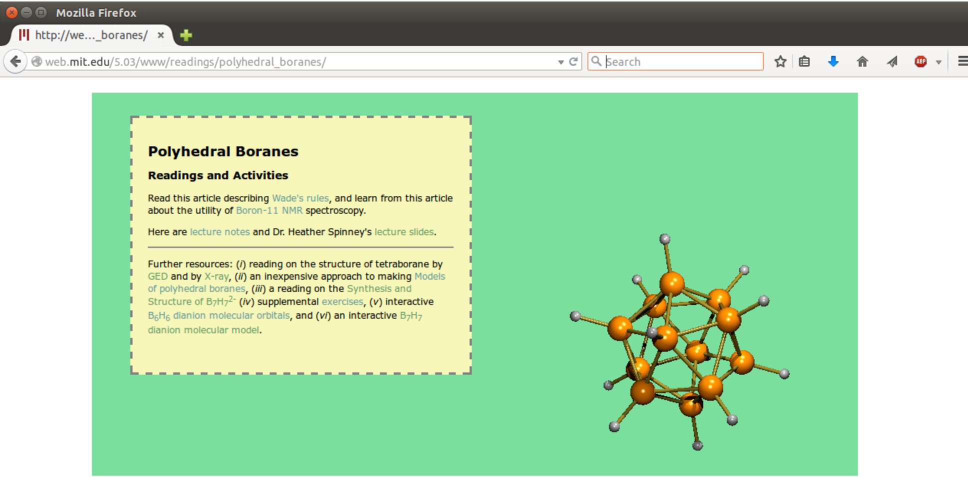


March 2015

Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
1	2 Polyhedral boranes	3	4 Boranes, Boron, BNCT	5	6 Nitrogen	7 2:00-4:00pm CCC office hours - location TBA
8	9 Phosphorus PSET 2 due in class (from BPR through N)	10	11 N versus P	12	13 Oxygen	14
15	16 Exam I (Evening, coverage: PSETS 1 and 2)	17	18 Sulfur	19	20 Noble gases	21
22	23 Spring Break	24 Spring Break	25 Spring Break	26 Spring Break	27 Spring Break	28
29	30 Transition Metal Complexes; Free Ion Terms	31			February S M T W T F S 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28	April S M T W T F S 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30

April 2015

Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday



Polyhedral Boranes

Readings and Activities

Read this article describing Wade's rules, and learn from this article about the utility of Boron-11 NMR spectroscopy.

Here are lecture notes and Dr. Heather Spinney's lecture slides.

Further resources: (*i*) reading on the structure of tetraborane by GED and by X-ray, (*ii*) an inexpensive approach to making Models of polyhedral boranes, (*iii*) a reading on the Synthesis and Structure of $B_7H_7^{2-}$ (*iv*) supplemental exercises, (*v*) interactive B_6H_6 dianion molecular orbitals, and (*vi*) an interactive B_7H_7 dianion molecular model.

Statement on Grading and Textbook

- Problem sets, 25%
- Exam 1, 20%
- Exam 2, 20%
- Final Exam, 35%

Textbook: Shriver and Atkins' *Inorganic Chemistry* 6th Edition

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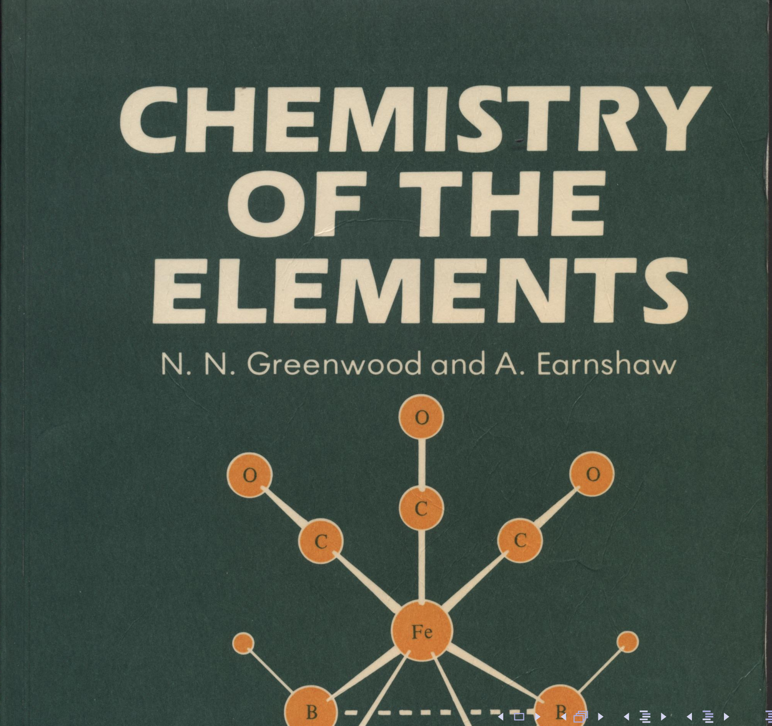
Periodic Table of the Elements

Key:

element name
atomic number
symbol
atomic weight (mean relative mass)

1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.38	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.96	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 **	lawrencium 103 Lr [262]	rutherfordium 104 Rf [267]	dubnium 105 Db [268]	seaborgium 106 Sg [271]	bohrium 107 Bh [272]	hassium 108 Hs [270]	meitnerium 109 Mt [276]	darmstadtium 110 Ds [281]	roentgenium 111 Rg [280]	ununbium 112 Uub [285]	ununtrium 113 Uut [284]	ununquadium 114 Uuq [289]	ununpentium 115 Uup [288]	ununhexium 116 Uuh [293]	ununseptium 117 Uus —	ununoctium 118 Uuo [294]

*lanthanoids	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.06
**actinoids	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]



CHEMISTRY OF THE ELEMENTS

N. N. Greenwood and A. Earnshaw


H
Li BE
Na mg
K Ca Sc Ti V Cr Mn Fe CO Ni Cu Zn
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd
Cs Ba Hf Ta W Re Os Ir Pt Au Hg
Fr Ra Rf Db Sg Bh Hs Mt Ds Rg Cn
B C N O F Ne
Al Si P S Cl Ar
Ga Ge As se Br
In Sn Sb Te I
Ti Po Bi Po At
Uut Uuq Uup Uuh UUS
LA CE Pr Nd Pm Sm Eu Gd Tb Dy HO Er Tm Yb Lu
AC Th Pa U Np Pu Am Cm Bk Cr Es Fm Md No Lr

The Cosmic Kitchen

- Snow is water, hydrogen and oxygen
- 10% of your body is hydrogen
- Hydrogen all comes from the Big Bang
- You are carrying the Big Bang within you!

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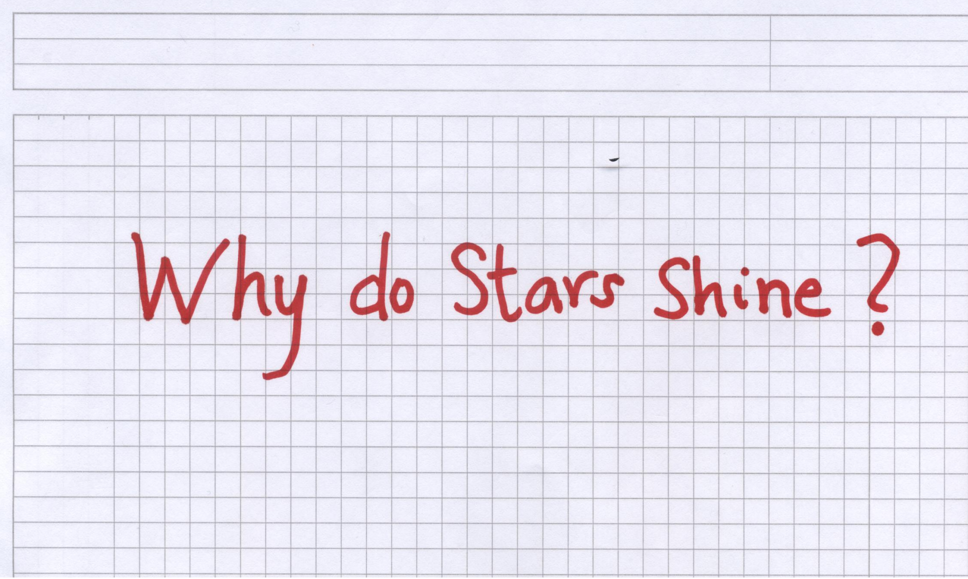

Why do Stars Shine ?

The Cosmic Kitchen

- Stars are 75% H, 24% He
- Stars are about 1% all other elements...
- This is roughly the chemical composition of the Universe

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- H is burning to He in the core of the star
- $E = mc^2$
- four protons weigh just a little bit more than the two protons and two neutrons of the He nucleus
- That mass (0.7%) is released as energy per reaction of He formation

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The Triple Alpha Reaction

- For 90% of the star's life it burns H to He
- ...then it has a He core
- He → C in the "triple alpha" reaction
- 3 He gives one C

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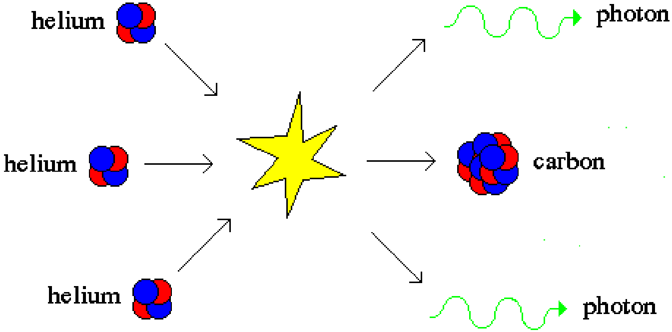
Triple Alpha Process

$$^{4}\mathrm{He}_2 + {}^{4}\mathrm{He}_2 + {}^{4}\mathrm{He}_2 \longrightarrow {}^{12}\mathrm{C}_6 + \gamma + \gamma$$



when stellar core temperatures exceed 100 million degrees, the triple alpha process starts where three helium nuclei are fused to form carbon and energy as photons

An Iron Core at the End

- As C begins to form, we are beginning to get new elements that were not present in the Universe at the beginning
- When a star gets older it goes through more burning stages
- Close to the end of a star's life it has onion-like layers with heavier elements closer to the core
- To keep shining, to sustain luminosity as it gets older, the star burns heavier and heavier elements
- This stops at Fe, the end stage is an iron core

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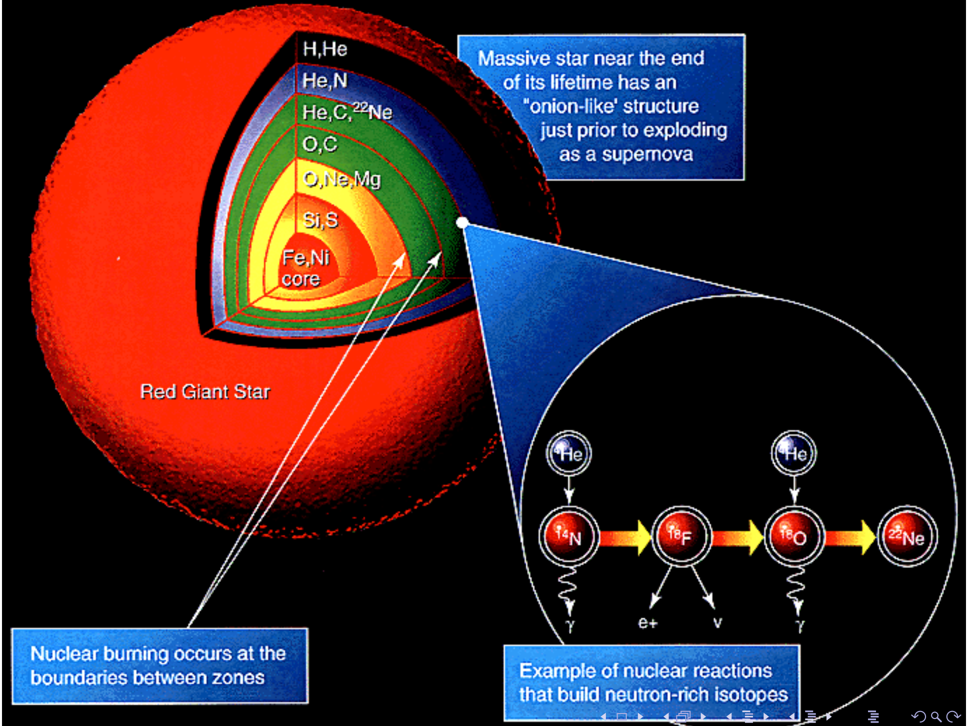
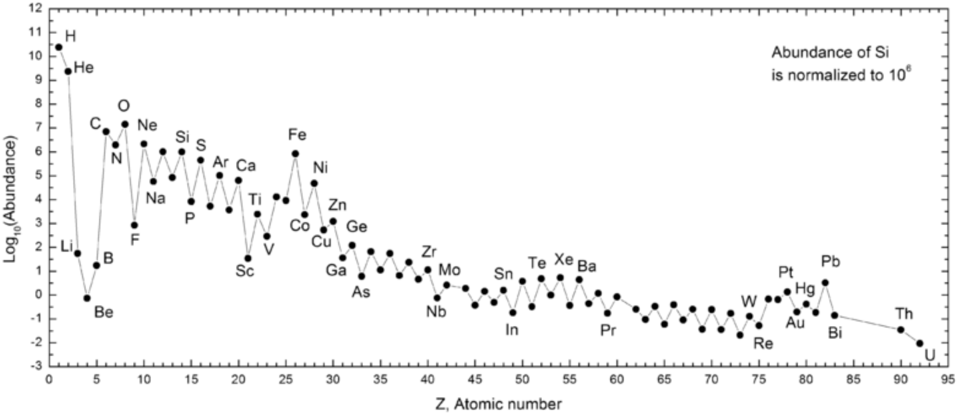


Massive star near the end of its lifetime has an "onion-like' structure just prior to exploding as a supernova

Nuclear burning occurs at the boundaries between zones

Example of nuclear reactions that build neutron-rich isotopes


Abundance of Si
is normalized to 10^6
Log$_{10}$(Abundance)
Z, Atomic number
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
H
He
Li
Be
B
C
N
O
F
Ne
Na
Si
P
S
Ar
Ca
Sc
Ti
V
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Zr
Nb
Mo
Sn
In
Te
Xe
Ba
Pr
W
Re
Pt
Au
Hg
Pb
Bi
Th
U

Chemical Evolution

- Age of the Universe: 13.8 billion years (Gyr)
- Big Bang left behind a “primordial universe” that was heavy-element free
- Today we have about 1-2% heavier elements
- The first stars were 10, 50, even 100 solar masses and eventually exploded in supernova
- Supernova creates a giant gas cloud containing the new elements

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1995 ▪ WFPC2

2014 ▪ WFC3/UVIS

M16 ▪ Eagle Nebula
Hubble Space Telescope

NASA and ESA ▪ STScI-PRC15-01a

Chemical Evolution

- We pass on DNA from one generation to the next
- Massive stars do the same thing in passing on their chemical composition that comes from burning and supernova
- Not all elements are created equal
- Big, massive stars are like gas guzzlers, not efficient with their nuclear fuel
- They get quickly to their iron core, and go boom!

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- Smaller stars could now form from the gas clouds of the first supernovae
- They may have 1 solar mass or less, and a long lifetime, ca. 10 Gyr
- Stars from this 2nd generation after the Big Bang are still around
- We can start to answer the question, which elements were formed in the 1st supernovae, and how much?

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- The sun has 1 solar mass by definition
- The sun (and its planets) formed from a gas cloud enriched in heavy elements by many generations of stars
- The Universe had to have 8 billion years of time to enrich with elements the gas cloud from which the sun was formed
- Life was not possible until cosmic chemical evolution had progressed to this point, providing the elements needed to form a planet such as Earth

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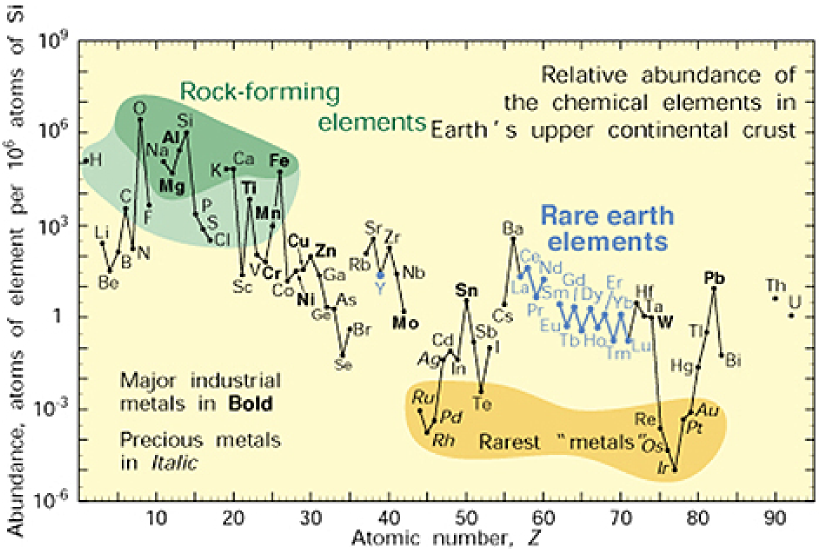
Relative abundance of
the chemical elements in
Earth's upper continental crust
Rock-forming
elements
Rare earth
elements
Major industrial
metals in **Bold**
Precious metals
in *Italic*
Rarest "metals"
Abundance, atoms of element per 10^6 atoms of Si
10^9
10^6
10^3
1
10^{-3}
10^{-6}
Atomic number, Z
10
20
30
40
50
60
70
80
90
H
Li
Be
B
C
N
O
F
Na
Mg
Al
Si
P
S
Cl
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Rb
Sr
Y
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Cs
Ba
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U

Back to the Periodic Table

- Elements in the columns have similar chemical properties
- Rows are more interesting from the standpoint of element creation
- H and He produced in the Big Bang at the beginning of space and time
- "Alpha elements" are built up by adding additional He nuclei: C → O → Ne
- Elements with odd atomic number (odd Z) are much harder to make; their formation is much less probable

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Back to the Periodic Table

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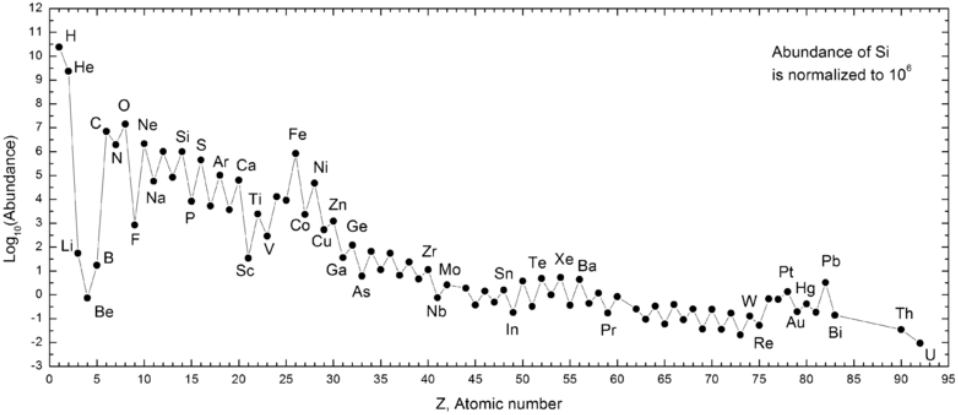
Abundance of Si
is normalized to 10^6
Log$_{10}$(Abundance)
Z, Atomic number
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
H
He
Li
Be
B
C
N
O
F
Ne
Na
Si
P
S
Ar
Ca
Sc
Ti
V
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Zr
Nb
Mo
Sn
In
Te
Xe
Ba
Pr
W
Re
Pt
Au
Hg
Pb
Bi
Th
U

The R Process

- Elements in the bottom part of the periodic table are formed in a very special process; getting to elements heavier than iron is kind of hard!
- Heavy elements are formed through neutron capture processes
- In a supernova there is a black hole and a neutron star being built up in the process; lots of neutrons around to impinge on an iron core!
- Thousands of neutrons impinge on an iron atom in around a second, generating a neutron-rich iron atom that is unstable and undergoes radioactive decay
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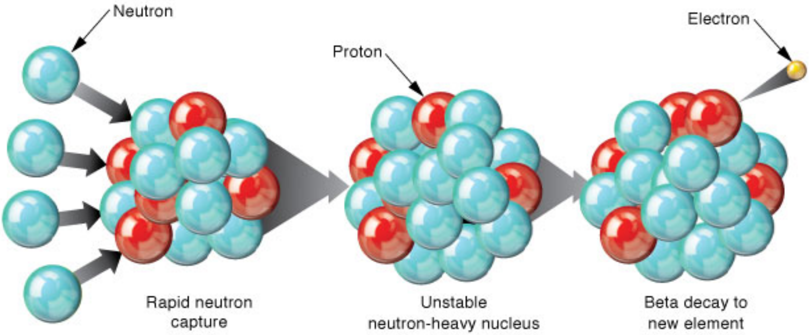
Neutron
Proton
Electron
Rapid neutron capture
Unstable neutron-heavy nucleus
Beta decay to new element

The S Process

- A similar but slow or “s process” of neutron capture happens in late stages of low mass stars
- They start pulsating and shed off their outer layer
- Neutron bombardment happens in a slightly less dramatic way than in the r process (supernova)

The S Process

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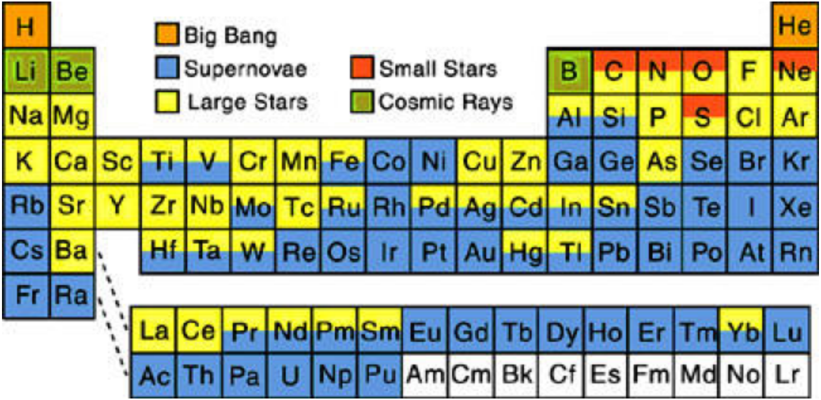
Periodic Table of Nucleosynthesis



The S Process

- Our sun formed from a gas cloud (pre-solar nebula) that was enriched by many r and s events
- Measurements allow determination of the relative contribution of r and s processes to the composition of the pre-solar nebula
- How do we determine the chemical abundances in stars?
- Spectroscopy, using starlight through a telescope! Every element absorbs at very specific wavelengths

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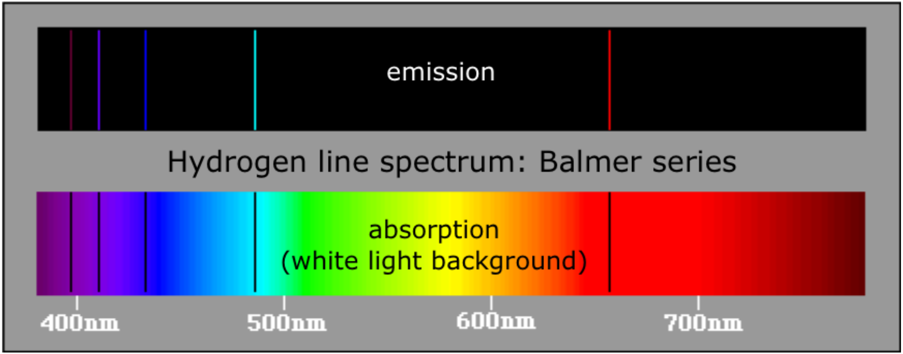
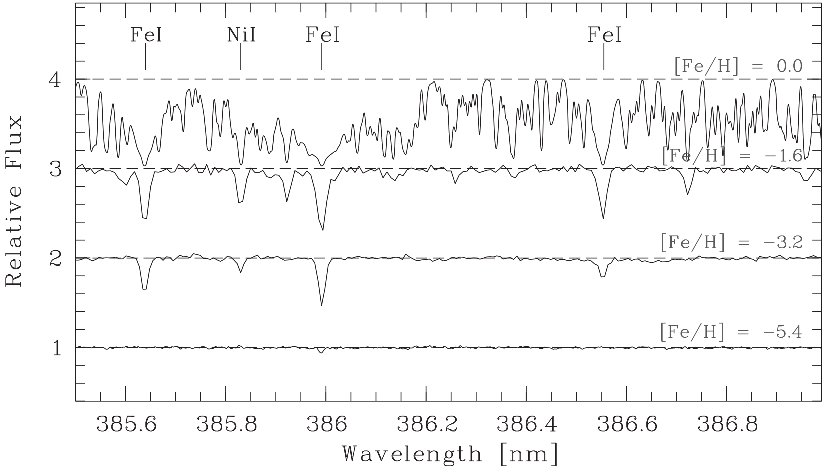
Balmer Series Line Spectra of Hydrogen



"Metallicity" Varies with the Age of Star



Window into the Early Universe

- Stars with low metallicity are much fewer in number compared to more metal-rich stars, reflecting the chemical evolution of the universe and also the overwhelming number of stars formed since its early stages
- Metal-poor stars are the only tool available to learn about the nature of the first stars and their supernova explosions

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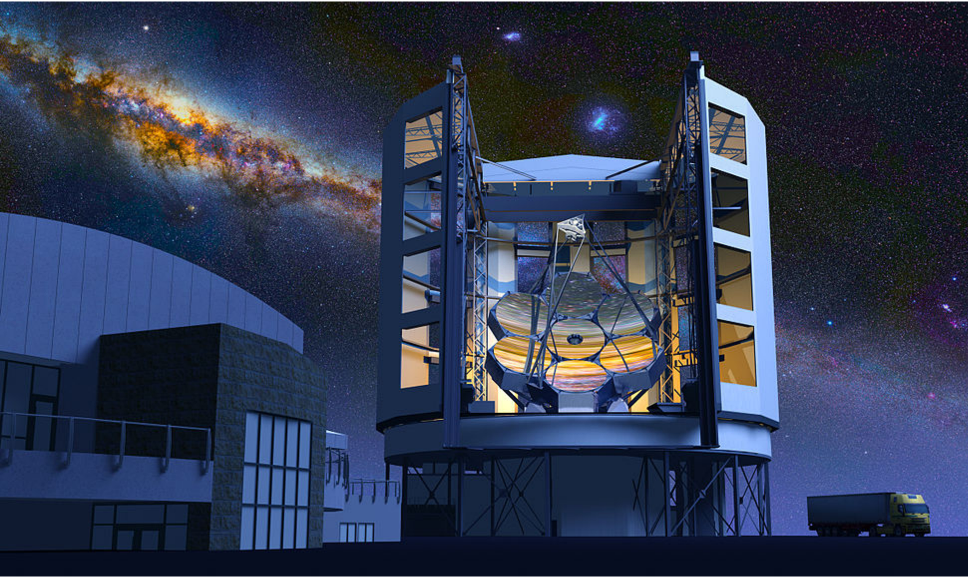
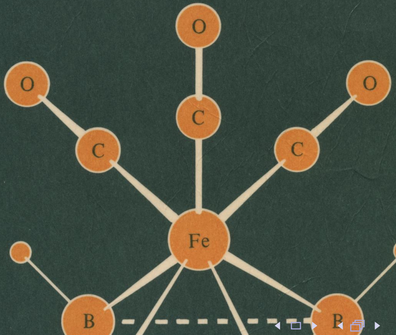
Giant Magellan Telescope



Prof. Anna Frebel, MIT Department of Physics

CHEMISTRY OF THE ELEMENTS

N. N. Greenwood and A. Earnshaw




H
Li BE
Na mg
K Ca Sc Ti V Cr Mn Fe CO Ni Cu Zn
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd
CS Ba Hf Ta W Re OS Ir Pt Au Hg
Fr Ra Rf Db Sg Bh Hs Mt Ds Rg Cn
B C N O F He Ne
Al Si P S Cl Ar
Ga Ge As se Br Kr
In Sn Sb Te I Xe
Tl Pb Bi Po At Rn
Uut Uuq Uup Uuh UUS
LA CE Pr Nd Pm Sm Eu Gd Tb Dy HO Er Tm Yb Lu
AC Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr