

Elements of Geochemistry

Highlights-

- Cosmic abundance of elements
- Oddo-Harkins rule
- Geochemical Classification of elements
- Co-ordination number, Pauling's rule

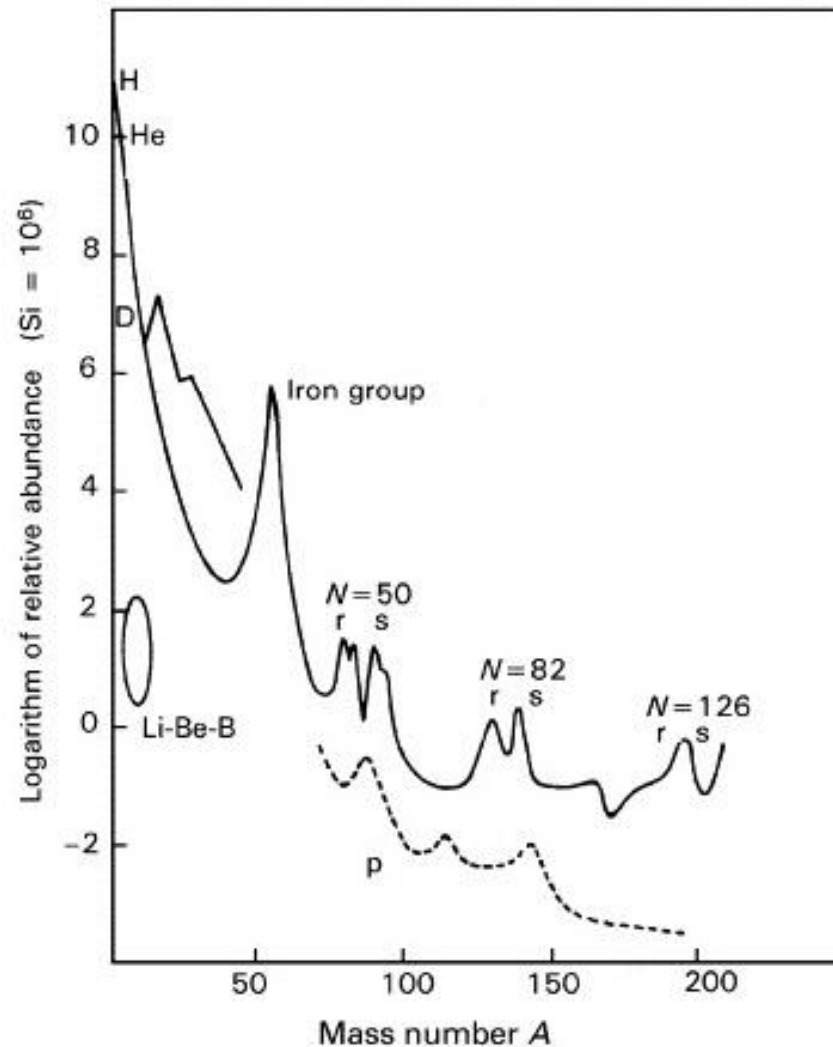
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- **Cosmic abundances of elements constrain the way in which the solar system evolves and dictate the composition of its members.**
- According to Nodac and Nodac cosmic abundance means cosmic abundance of materials in the solar system and stars of our own galaxy.



Cosmic abundance curve

COSMIC ABUNDANCE

The most abundant element in **the universe** is hydrogen, which makes up about three-quarters of all matter! Helium makes up most of the remaining 25%. Oxygen is the third-most abundant element in the universe. All of the other elements are relatively rare.

According to education site Vision Learning **Earth's atmosphere** is composed of approximately 78 percent nitrogen, 21 percent oxygen, 0.93 percent Argon, 0.04 percent carbon dioxide as well as trace amounts of neon, helium, methane, krypton, ozone and hydrogen, as well as water vapor.

Earth as a whole: iron (32.1%), oxygen (30.1%), silicon (15.1%), magnesium (13.9%), sulfur (2.9%), nickel (1.8%), calcium (1.5%), and aluminium (1.4%); with the remaining 1.2% consisting of trace amounts of other elements.

❖ The chemical composition of Earth is quite a bit different from that of the universe. The most abundant element in the **Earth's crust** is oxygen, making up 46.6% of Earth's mass. Silicon is the second most abundant element (27.7%), followed by aluminum (8.1%), iron (5.0%), calcium (3.6%), sodium (2.8%), potassium (2.6%), and magnesium (2.1%). These eight elements account for approximately 98.5% of the total mass of the Earth's crust.

❖ **Mantle:** oxygen 45%, magnesium 23%, silicon 22%, iron 5.8%, calcium 2.3%, aluminium 2.2%, sodium 0.3%, potassium 0.3%.

❖ Due to mass segregation, the **core of the Earth** is believed to be primarily composed of iron (88.8%), with smaller amounts of nickel (5.8%), sulfur (4.5%), and less than 1% trace elements.

➤ Relative abundance of **non-volatile elements** (in decreasing order):

O, Si, Al, Fe, Ca, Na, K, Mg

➤ Elementary abundance of **Meteorite** (in decreasing order):

O, Fe, Si, Mg, S, Ni, Al, Ca

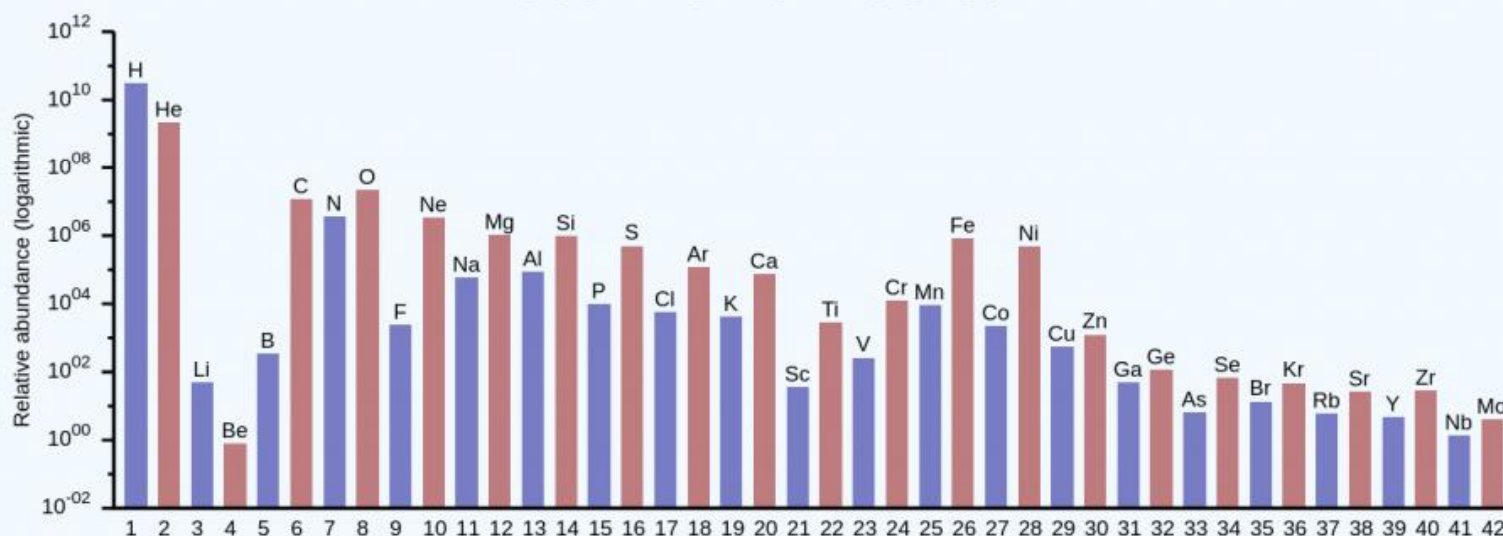
➤ Elementary abundance in **Sun** (in decreasing order):

H, He, O, Fe, Mg, Ni, Si, C

Guisepppe Oddo in 1914 and William Draper Harkins in 1917.

Oddo-Harkins Rule

The Oddo-Harkins rule states that the abundance of elements with even atomic numbers is greater than the abundance of adjacent elements with odd atomic numbers.



Exceptions to the rule are hydrogen and beryllium.

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For example, oxygen (atomic number 8) is more abundant than either nitrogen (atomic number 7) or fluorine (atomic number 9). Calcium (20) is more abundant than potassium (19) or scandium (21).

Explanation of the Oddo-Harkins Rule:

Atoms form when protons and neutrons bind together and form an atomic nucleus. For most elements, this happens when the immense temperature, pressure, and gravity within a star fuses protons and neutrons together. An element's atomic number is the number of protons in its atom.

❑ One explanation for the higher abundance of even-numbered elements is that helium (atomic number 2) is a major building block for element formation. Fusion of helium nuclei builds subsequent even atomic number elements.

❑ Another explanation is that even atomic numbers mean protons are paired within the nucleus. Parity makes the nucleons more stable, as the spin of one proton offsets the spin of the other. Unpaired protons (odd number elements) more easily capture another proton and form an even-numbered atom.

Chemists and astronomers see the Oddo-Harkins rule in action when massive stars die and explode. While different stars uphold the rule, their element ratio differs according to the metallicity of the star.

Exceptions to the Oddo-Harkins Rule

Elements that serve as two exceptions to the Oddo-Harkins rule are hydrogen (atomic number 1) and beryllium (atomic number 4).

Hydrogen is the most abundant element in the universe. It is more abundant than helium because of its creation in the Big Bang. However, stars continuously fuse hydrogen into helium. In the distant future, hydrogen will follow the even-odd rule.

Beryllium is even more rare than lithium (atomic number 3) and boron (atomic number 5), even though the primary source of the all three elements is cosmic ray spallation. Scientists believe beryllium does not follow the rule because it only has one stable isotope. Lithium and boron each have two stable isotopes.

GEOCHEMICAL CLASSIFICATION OF ELEMENTS:

➤ Proposed by **Victor Goldschmidt** (1888–1947)

➤ Groups the chemical elements within the Earth according to their preferred host phases

1. **Lithophile** (rock-loving; affinity for O and S)
2. **Siderophile** (iron-loving; affinity for Fe)
3. **Chalcophile** (sulfide ore-loving; affinity for S)
4. **Atmophile** (gas-loving)

Some elements have affinities to more than one phase.

Example: Cr is strongly lithophile element but also occurs in Fe meteorites as Daubreelite (FeCr_2S_4). Because meteorites form in low oxygen environment, Therefore Cr can not combine with O_2 but with S. So, Cr can also occur as chalcophile elements.

Goldschmidt classification in the periodic table

	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	*	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		
Goldschmidt classification:				Lithophile	Siderophile	Chalcophile	Atmophile	Trace/Synthetic											

Coordination number, also called Ligancy, the number of atoms, ions, or molecules that a central atom or ion holds as its nearest neighbors in a complex or coordination compound or in a crystal. tetra carbonyl nickel $\text{Ni}(\text{CO})_4$ has a coordination number of 4 as 4 CO ligands are attached to Ni atom.

*The arrangement of atoms in a crystal structure not only depends on the charge on the ion and type of bonding between atoms, but also on the size of the atoms or ions. In any given molecule or crystal structure each atom or ion will be surrounded by other atoms or ions. The number of ions or atoms that immediately surround an atom or ion of interest is called the **coordination number**, - **C.N.***

The coordination number depends on the relative size of the atoms or ions.

High temperature and low Pressure favors lower C.N.

Low temperature and high Pressure favors higher C.N.

Radius ratio	Arrangement of anion around cation	C.N. of cations
0.15-0.22	Corners of a equilateral triangle	3
0.22-0.41	Corners of a tetrahedron	4
0.41-0.73	Corners of a octahedron	6
0.73-1	Corners of a cube	8
1	Closest packing	12

Pauling's Rules

Linus Pauling studied crystal structures and the types of bonding and coordination that occurs within them. His studies found that crystal structures obey the following rules, now known as Pauling's Rules.

Rule 1

Around every cation, a coordination polyhedron of anions forms, in which the cation-anion distance is determined by the radius sums and the coordination number is determined by the radius ratio.

This rule simply sets out what we have discussed above, stating that the different types of coordination polyhedra are determined by the radius ratio, R_x/R_z , of the cation to the anion.

Rule 2, The Electrostatic Valency Principle

An ionic structure will be stable to the extent that the sum of the strengths of the electrostatic bonds that reach an ion equal the charge on that ion.

In a stable structure the total strength of the valency bonds which reach an anion from all the neighboring cations is equals to the charge of the anions. This expresses the tendency of any structure to assume a configuration of minimum potential energy whereby the charges on the ions are as far as possible neutralized by their immediate neighbors.