

Introduction

Group 3 of the periodic table contains scandium, yttrium and lanthanum. Strictly speaking, actinium should also be included, but in practice, it is studied separately. There are fourteen elements that follow lanthanum and these are called lanthanides. The lanthanides comprises of the largest occurring group in the periodic table. These lanthanides are placed below the main body of the periodic table in the manner of a footnote. The full-width version of the periodic table shows the position of the lanthanides more clearly (Table 1).

Table 1: Modern Periodic Table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La [*]	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac ^{**}	Rf	Db	Sg	Bh	Hs	Mt	Uu	Uu	Uu	Uu	Uu	Uu	Uu	Uu	Uu
Lanthanoids^{**}			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Actinoids^{**}			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

These lanthanides are associated with a major confusion regarding their terminology. Whether the term "Lanthanides" refers to the fifteen elements from La to Lu or the fourteen elements from Ce to Lu has been debated for long. "Rare Earth Elements" and "Rare Earth Metals" are trivial names sometimes applied to a collection of these elements in the periodic table. Earth is an obsolete term for "oxide". At the time of their discovery, the oxides of these elements were believed to be scarce in abundance, as minerals. This terminology is no longer appropriate, as these elements are no longer rare, except promethium, with a $t_{1/2}$ of 2.6 years. To avoid any confusion, now the term "lanthanoid" rather than "lanthanide", is used to represent these elements as the suffix "-ide" is generally used to indicate anions. However, even now there is a confusion regarding the position of La, i.e., whether the group is made up of fifteen elements, La to Lu, or fourteen elements, Ce to Lu. Lanthanides are chemically similar to each other, to scandium as well as yttrium. Currently, the general symbol, Ln, is used for the fourteen elements (Ce - Lu) and group III elements Sc, Y and La.

The story of the lanthanoids begins in 1787 when a young Swedish artillery officer, Lieutenant Carl Axel Arrhenius, who was a keen amateur geologist, was exploring a quarry at a small town called Ytterby, near Stockholm. He found a new, very dense black mineral which he named ytterbite. Its chemical analysis carried out by Johan Gadolin, a Finnish chemist in 1794 showed that the new mineral contained oxides of iron, beryllium, silicon and a new, previously unidentified 'earth' which he named 'yttria'. Yttria was later shown to be a mixture of the oxides of six rare earth elements. The history of discovery and naming of the lanthanides are summarized in Table 2.

Table 2: Discovery & origin of names of lanthanoids, including yttrium, thorium & scandium

Year	Element	Origin of name	Discoverer	Nationality	Comments
1794	Yttrium	Ytterby mine, Sweden	Johan Gadolin	Finn	
1803	Cerium	After the asteroid Ceres (which in turn named after a Greek deity)	Baron Jons Jakob Berzelius and William Hisinger	Swedish	Also discovered independently in same year by Martin Heinrich Klaproth (German). The pure element was not isolated until 1875.
1828	Thorium	After Thor, the Scandinavian god of war	Baron Jons Jakob Berzelius	Swedish	
1839	Lanthanum	From Greek lathano = to lie hidden (because it lay concealed in the earth)	Carl Gustav Mosander	Swedish	
1843	Erbium	Derived from Ytterby mine, Sweden	Carl Gustav Mosander	Swedish	
1878	Terbium	Derived from Ytterby mine, Sweden	Carl Gustav Mosander	Swedish	
1878	Ytterbium	Derived from Ytterby mine, Sweden	Jean Charles de Marignac	French	In 1907 and 1908, Georges Urbain (French) and Carl Auer Von Welsbach (Austrian) independently separated Marignac's ytterbium into two elements, which are now called ytterbium and lutetium
1879	Samarium	After the mineral samarskite, in turn after the minerals discoverer, a Russian mining official V. E. Samarsky	Paul E. Lecoq de Boisbaudran	Swedish	

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1879	Scandium	After Scandinavia	Lars Fredrik Nilson	Swedish	
1879	Holmium	After the Latin word for Stockholm, Holmia	Per Teodor Cleve	Swedish	Also discovered independently by Jacques Louis Soret and Marc Delafontaine (Swiss)
1879	Thulium	From the Latin Thule, an ancient name for Scandinavia	Per Teodor Cleve	Swedish	
1880	Gadolinium	In the honour of Johan Gadolin, a Finnish chemist	Jean Charles de Marignac	Swiss of French origin	Paul E. Lecoq de Boisbaudran independently isolated the element from Mosander's yttria in 1886
1885	Praseodymium	From Greek prasios = green, in reference to the colour of the salts and didymos = twin, because the earth didymia was separated into two salts; Pr and Nd	Carl Auer Von Welsbach	Austrian	
1885	Neodymium	From Greek neo = new and didymos = twin, because the earth didymia was separated into two salts; Pr and Nd	Carl Auer Von Welsbach	Austrian	Not isolated in relatively pure form until 1925
1886	Dysprosium	From Greek dys = bad and prositos = approachable, dysprositos means hard to get because of the difficulty involved in its detection and isolation	Paul E. Lecoq de Boisbaudran	French	
1	Europium	After Europe	Eugene Demarcay	French	

1907	Lutetium	After Lutetia , Latin name for the place where Paris was founded	Independently by Georges Urban and Carl Auer Von Welsbach	French and Austrian	
1947	Promethium	After Prometheus , in greek mythology , who brought fire to mankind in reference to harnessing of the energy of the nuclear fission and warning against its dangers	Charles DuBois Coryell Lawrence E. Glendenin and Jacob A. Marinsky	American	

On the basis of their separability, the lanthanoids were conveniently divided into the "cerium group minerals" or "light earths" (including light lanthanoid elements, from La to Euro) and the "yttrium group minerals" or "heavy earths" (including heavy lanthanoid elements from Gd to Lu, along with Y). Yttrium is lighter than other "yttrium group minerals", but is still grouped with them, as it has a comparable ionic radius and occurs in nature associated with the ores of heavier lanthanoids. This unit shall deal with the general chemistry of lanthanoids, including the implementation of the conceptual approach. The unit also provides the background essential to understand the problems of their recovery and separation, along with their applications.

Position of Lanthanoids in the Periodic Table

The lanthanoids have atomic numbers between those of barium ($Z = 56$) and hafnium ($Z = 72$), and hence must be placed between these two elements. Ba is an alkaline earth metal belonging to group 2, below Sr. Hf is present in group 4, below Zr, thus leaving only one place between them, which lies exactly below Y ($Z = 39$, group 3).

Since all the lanthanoids resemble each other in many aspects, therefore it became necessary to accommodate all of them together at one place. This problem is solved by placing the first element i.e. La below Y and the remaining elements separately in the lower part of the periodic table (Table 1).

Terrestrial Abundance and Distribution

The lanthanoid elements are not particularly rare. Apart from the unstable ^{147}Pm (half life 2.6 years) of which traces occur in uranium ores, all the lanthanoids are actually more abundant than iodine. Cerium is the twenty-sixth most abundant of all elements, being half as abundant as Cl and more abundant than lead. Even Tm, the rarest after Pm, is more abundant than iodine, and Lu is more abundant than gold. The abundance of these elements and the number of naturally occurring isotopes vary regularly, in accordance with Harkins' rule (Table 3).

Table 3: Abundance of the lanthanoides in the earth's crust by mass and number of natural isotopes

Atomic number	Element	Abundance (ppm) in earth's crust	Relative abundance	Naturally occurring isotopes
58	Ce	66	26	4
59	Pr	9.1	37	1
60	Nd	40	27	7
61	Pm	0		0
62	Sm	7.0	40	7
63	Eu	2.1	49	2
64	Gd	6.1	41	7
65	Tb	1.2	56	1
66	Dy	4.5	42	7
67	Ho	1.4	55	1
68	Er	3.5	43	6
69	Tm	0.5	61	1
70	Yb	3.1	44	7
71	Lu	0.8	59	2

According to this rule, the elements with even atomic numbers are more abundant and have more stable isotopes, than those with odd atomic numbers. The graphical representation of their abundance is given in fig 1.

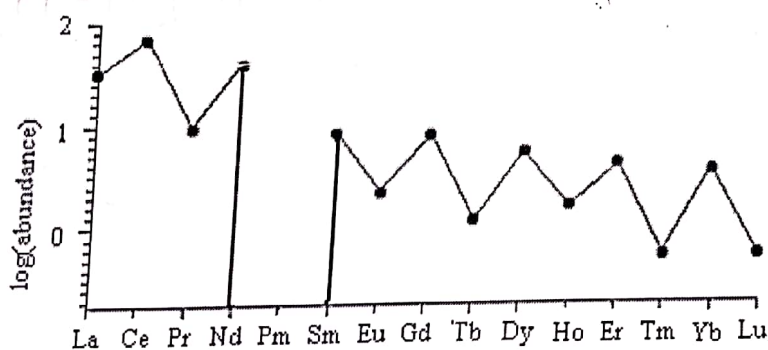


Fig. 1: Abundance of Lanthanoids in Earth's crust

The non-existence of promethium in nature may be explained by Mattauch's rule. This states that if each of the two elements with consecutive atomic numbers have an isotope of the same atomic mass, one of the isotopes will be unstable. Since Nd ($Z = 60$) has stable isotopes with mass numbers 142, 143, 144, 145, 146, 148, 150 and 152 and Sm ($Z = 62$) has the isotopes with mass numbers 144, 147, 148, 149, 150, 152 and 154, there are not many stable mass numbers available for promethium ($Z = 61$). If Pm is to have a stable isotope, it must have a mass number outside the range 142 - 150. The isotopes of Pm which have been identified so far are radioactive.

Many minerals are known to contain lanthanoids (Table 4). The symbols Ce and Y in the table represent the elements in cerium group and yttrium group, respectively. Out of the list of the mentioned minerals, only two, namely, monazite and bastnaesite are of commercial importance. Monazite is sparsely distributed in various rocks but, due to its high density and inertness, it is concentrated by weathering into sand or beaches, usually in the presence of other similar minerals such as cassiterite (SnO_2). Their rich deposits occur in Travancore, South Africa, Brazil, Malaysia, the U.S.A and Australia. In fact, before 1960, monazite was the only source of lanthanoids. However, a vast deposit of bastnaesite was explored in the Mountain Pass, California has since then become the most important single source of lanthanoids. Apart from the U. S. A. it is also found in Madagascar.

Table 4: Important Minerals of Lanthanoids

Minerals	Composition	Location of significant deposits
	(1) Cerium group minerals	
(i) Monazite Sand- Mixture of orthophosphates of Ce-earths, $(\text{Ce})\text{PO}_4$	50-70% Ce-earths (i.e. elements of at. no. 57 to 62 calculated as oxides) 1-4% Y-earths (i.e. elements of at. no. 63 to 71 calculated as oxides) 5-10% ThO_2 1-2% SiO_2 22-30% P_2O_5 Traces of U	Occurs in the sand beaches of Travancore (India) Brazil South Africa U.S.A.
(ii) Bastnaesite-cerium earth fluorocarbonate, $(\text{Ce})\text{FCO}_3$	65-70% Ce-earths, < 1% Y-earths	Sweden, California, New Mexico
(iii) Cerite-A hydrated silicate of the composition, $(\text{Ce})_3 \text{M}^{\text{II}} \text{H}_3 \text{Si}_3 \text{O}_{11} (\text{M}-\text{Ca}, \text{Fe})$	Traces of thorium 51-72% Ce-earths 7.6% Y-earths Traces of Th, U, Zr	Sweden Caucasus
	(2) Yttrium group minerals	
(i) Gadolinite or Ytterbite- A yttrium-earth, iron and beryllium silicate, $(\text{Ce}, \text{Be})_3 (\text{Y}_2) \text{Si}_2 \text{O}_{10}$	35-48% Y-earths (Calculated as oxides) 2-17% Ce-earths Upto 11.6% BeO Traces of ThO_2	Sweden, Norway USA (Texas and Colorado)
(ii) Xenotime - An orthophosphate of Y-earth (analogous to Monazite), $(\text{Y})_2 \text{PO}_4$	54-65% Y-earths ~ 0.1% Ce-earths Upto 3% ThO_2 , upto 3.5% U_3O_8 2-3% ZrO_2	Norway Brazil
(iii) Euxenite- Mixture of titanates, niobates and tantalates of Y-earths, $(\text{Nb}, \text{Ta}) \text{TiO}_6 \cdot \text{XH}_2\text{O}$	13-35% Y-earths (Calculated as Oxides) 2-8% Ce-earths (Calculated as Oxides) 20-23% TiO_2 , 25-35% $(\text{Nb}, \text{Ta})_2\text{O}_5$	Australia, Idaho (U.S.A.)

chlorides. The solution is then treated with a solution of BaCl_2 and $\text{Ln}_2(\text{SO}_4)_3$ in stoichiometric amounts. BaSO_4 precipitates out, along with radioactive ^{228}Ra as RaSO_4 . This scheme is summarized in fig.2 (b). The remaining solution containing Ln and lanthanoid chlorides can be used to separate the individual components by special techniques.

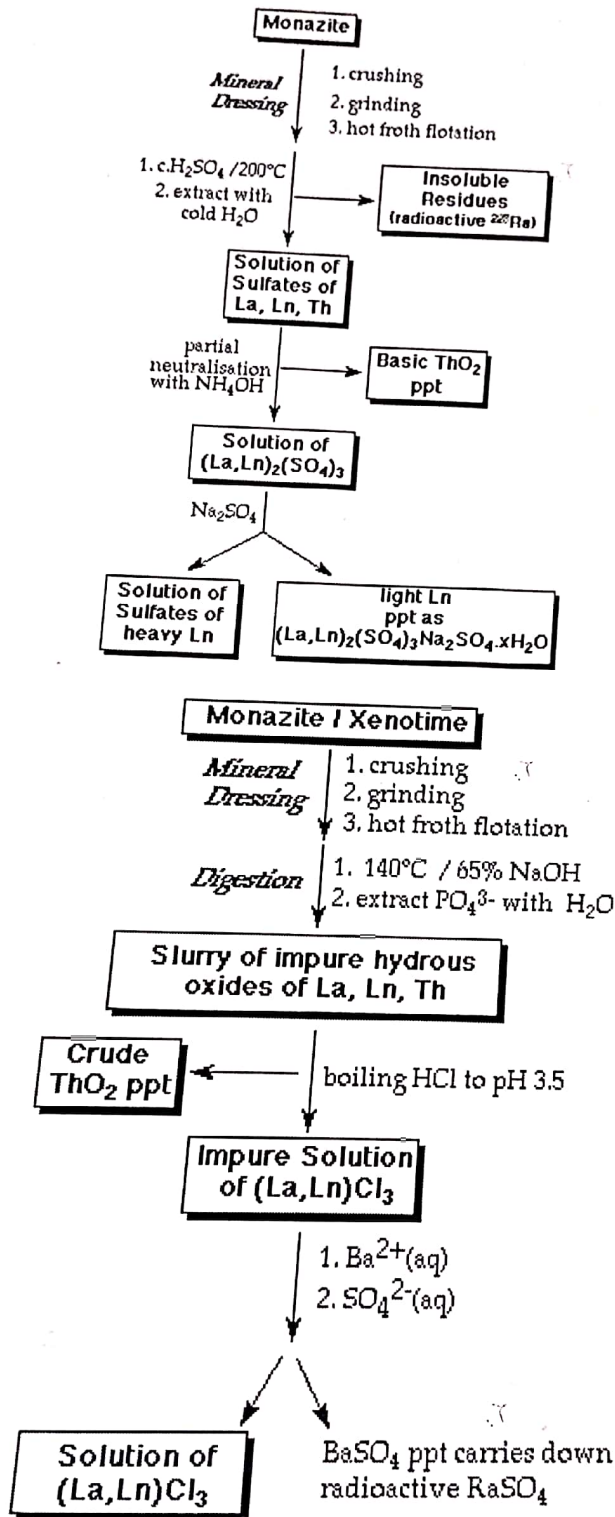


Fig. 2: Cracking of Monazite / xenotime by (a) conc. H_2SO_4 ; (b) NaOH

...Cracking methods, the conc. H₂SO₄ treatment is more economical than the separation process. However, the latter process gives higher yields and a cleaner separation.

(iii) **Cracking of bastnaesite** - The bastnaesite mineral contains very small amounts of Th and heavy lanthanoids and requires a comparatively simpler treatment. The concentrated ore is treated with conc. H₂SO₄ at 200°C, when CO₂, HF and SiF₄ are evolved. The dried product is then treated with water to obtain a solution containing lanthanum and the light lanthanoids, which are then separated out via special techniques discussed later in the unit. A schematic representation of the procedure followed is given in fig 3.

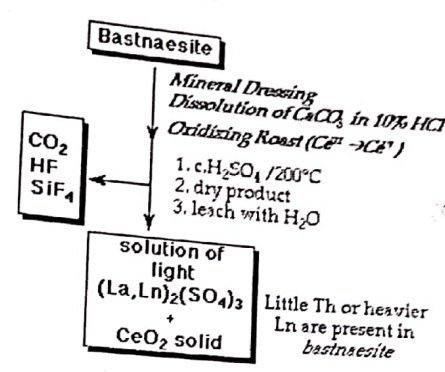


Fig.3: Cracking of Bastnaesite

Electronic Structure

The electronic structure of the members of group 3, in the modern periodic table, indicates that the elements usually listed in this family are the first members of the four d-type transition series.

- Sc, Z = 21 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹ 4s²
Or, [Ar] 3d¹ 4s²
- Y, Z = 39 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s² 4p⁶ 4d¹ 5s²
Or, [Kr] 4d¹ 5s²
- La, Z = 57 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s² 4p⁶ 4d¹⁰ 5s² 5p⁶ 5d¹ 6s²
Or, [Xe] 5d¹ 6s²
- Ac, Z = 89 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s² 4p⁶ 4d¹⁰ 4f¹⁴ 5s² 5p⁶ 5d¹⁰ 6s² 6p⁶ 6d¹ 7s²
Or, [Rn] 6d¹ 7s²

In elements succeeding scandium and yttrium, the electrons are added to the 3d and 4d levels respectively, giving the first and the second transition series. However, after lanthanum, the energy of the 4f level falls below that of the 5d and thus the electrons are added to the inner, well-shielded 4f orbitals before entering into the 5d subshell. Hence, the lanthanoid series is defined by the progressive filling of the 4f

At present, China is estimated to have the world's largest deposits of lanthanides (43%) and is now the largest producer of these elements. India contributes only 3% towards the production of lanthanoids. Promethium is not available from rare earth ores. It occurs only in traces in uranium ores where it is formed by spontaneous fission of ^{238}U . It was first isolated as ^{147}Pm by exchange methods from products of nuclear fission reaction.

Extraction of Lanthanoids from Minerals

The distribution of the lanthanoids in the two commercially important minerals, monazite and bastnaesite, is quite similar. Both these minerals contain metals such as Ce, La, Nd and Pr. However, monazite typically contains 5–10% ThO_2 and 3% yttrium earths, which are almost absent in bastnaesite. The complex composition makes the chemical treatment of monazite very extensive and lengthy. Moreover, though thorium is only weakly radioactive, it is contaminated with daughter elements such as ^{228}Ra which are more active and hence require careful handling during the processing of monazite.

Processing includes cracking the minerals, recovering the lanthanoids (along with thorium), removing thorium if present and separating the lanthanoids. The concentration of the mineral usually begins with gravity separation on Wilfley table. Since these minerals are heavy, their sand gets caught up on the riffles and the gangue material is washed off and dried. The magnetic impurities are removed by magnetic separation.

The concentrated mineral is then subjected to chemical treatment, which is technically known as "opening up" or "cracking". These treatments depend on the ore being used and the extent to which the metals are to be separated from each other. The chemical treatment of monazite is done either by NaOH or concentrated H_2SO_4 solution. The principle underlying the cracking is the difference in solubilities of $\text{Ln}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ for the light and the heavy lanthanoids and also the low solubility of the hydrous oxide of thorium.

(i) **Cracking of monazite by conc. H_2SO_4** – The finely powdered and concentrated ore is treated with 93% H_2SO_4 at 200°C for several hours. The reaction is exothermic and the resulting viscous paste is leached with cold water. Th, La and the lanthanoids dissolve as sulphates, leaving behind the insoluble residues which mainly contain radioactive ^{228}Ra . The solution of sulphates of Th, La and Ln, on partial neutralization with NH_4OH , precipitates out ThO_2 . The remaining solution is then treated with Na_2SO_4 , to salt out La and the light lanthanoids as sulphate, leaving the heavy lanthanoids in solution. This scheme is summarized in fig.2 (a). The solution containing the sulphates of heavy lanthanoids can then be used to separate the individual components by various methods, such as valency change, ion exchange and solvent extraction, discussed later in the unit.

(ii) **Cracking of monazite by NaOH** – The finely powdered and concentrated ore is treated with 65% NaOH solution at 140°C , followed by extraction with water. A slurry of impure hydrous oxides is obtained, which is treated with boiling aq. HCl until the pH is 3.5. Crude ThO_2 separates out leaving behind a solution of impure lanthanoid

THE *f*-BLOCK ELEMENTS

Lanthanides

The elements in which the additional electron (also called differentiating electron) enters $(n-2)f$ orbitals are called *f-block elements*. Since $(n-2)f$ orbitals lie comparatively deep within the kernel (being inner to the penultimate shell), these elements are also called **inner transition elements**. These $(n-2)f$ orbitals may be either $4f$ -orbitals or $5f$ -orbitals. Depending on whether the additional electron enters $4f$ or $5f$ -orbitals, *f*-block elements have been classified into two blocks namely (i) $4f$ -block elements and (ii) $5f$ -block elements. The $4f$ -block elements are also called **1st inner-transition series elements, lanthanides, lanthanones or rare earths**. The $5f$ -block elements are also called **2nd inner-transition series elements, actinides or actinones**. The valence-shell electronic configuration of *f*-block elements can be represented as: $(n-2)f^{0,2-14} . (n-1)d^{0,1,2} . ns^2 (n=6 \text{ or } 7)$

12.1 Lanthanides

The fifteen elements from lanthanum to lutetium (At. no 57 to 71) are called *lanthanides*. Strictly speaking, the first member La_{57} (configuration $6s^2 5d^1 4f^0$) and the last member Lu_{71} ($4f^{14} 5d^1 6s^2$) have no partially filled $4f$ orbital in their ground state yet they are considered to belong to lanthanide series because their chemical properties are very closely similar to the other thirteen elements of the series. Thus strictly according to this definition of lanthanides only *thirteen* elements from Ce_{58} ($4f^2 5d^0 6s^2$) to Yb_{70} ($4f^{14} 5d^0 6s^2$) should be the members of lanthanide series. In fact the name *lanthanides* has been derived from lanthanum which is the *prototype* of lanthanides.

12.2 Position of Lanthanides in the Periodic table. All the fifteen lanthanides have atomic numbers between those of Ba ($Z=56$) and hafnium ($Z=72$) and, therefore, must be placed between these two elements as was also proved by Mosely. Ba has exactly the same outer electronic configuration as Ca and Sr and resembles them very closely. In a similar way hafnium is similar to zirconium ($Z=40$). Therefore Ba must be placed below Sr (Group IIA i.e., Group 2) and Hf below Zr (Group IVB i.e. Group 4), thus leaving only one place between them, which lies exactly below Y ($Z=39$, Group IIIB i.e., Group 3).

Since all the fifteen lanthanides resemble one another in many respects, these must be placed in the same group. These elements also resemble Y₃₉. It, therefore, become necessary to accommodate all the fifteen lanthanides together at one place. This has been done by placing the first element $_{57}\text{La}$ below $_{39}\text{Y}$ and remaining fourteen elements (i.e., $_{58}\text{Ce}$ to $_{71}\text{Lu}$) have been placed separately in the lower part of the periodic table.