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**GEOCHEMISTRY OF IRON ORES**

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**INTRODUCTIO**

Geochemical process of selective concentration of elements is controlled by the dynamic tectonic evolution of earth in the geological time scale of million of years. Iron crystallizes out from magmatic melt if the evolved basaltic melt is highly enriched with Fe (high chemical activity of Fe) and suitable pressure temperature (thermodynamic) condition to stabilize spinel magnetite and ilmenite. Iron is soluble in atmospheric Eh-pH conditions and is amenable to precipitate as hydroxide, oxyhydroxide, carbonate and sulphide in localized change in Eh-pH. The silicate minerals weather to release Fe which precipitates as goethite, chamosite, siderite, pyrite in sedimentary geochemical environment depending upon the low-temperature thermodynamics prevailing in the depositional site. The phase transition to magnetite and hematite is also possible during metamorphism and martitisation. So, concentration of iron in geological set up can occur in widely varied conditions from lacustrine to marine, even magmatic to metamorphic. While sedimentary iron deposit is associated with sedimentary rocks and to their metamorphic equivalent in case the terrain is metamorphosed, the magmatic iron deposit is associated with basalt and metabasalt. It is also suggested that hydrothermal action can selectively leach out carbonate-silicate metasediments with supergene enrichment of Fe. Majority of the iron ore deposits (Fig.- 5.1) are confined to Banded iron formation (BIF) of Proterozoic volcano-sedimentary sequence (supracrustal) of age 2.5-2.4Ga, 2.2 - 2.06Ga and 2.0Ga. Thus, Complex genetic process has a control over the mineralogical and geochemical attribute of the iron ore, associated rocks and their host rocks. The associated rocks contribute to the gangue component, which is the interest of Mineral Engineering to get rid of. The geochemical data also helps to understand the ore, its utility and recovery of valuable metals if any.

**IRON ORE TYPES**

The term ore is applied to a geological litho unit where the element content is anomalously high enough so that the metal can be recovered with profit. Depending upon the resource availability in a country and the gap in demand and supply, iron ores of different types find economic importance. Following types of iron ore are identified out of which iron ore hosted by banded iron formation and magmatic magnetitic ore are of commercial significance, and will be discussed in details in the following sections.

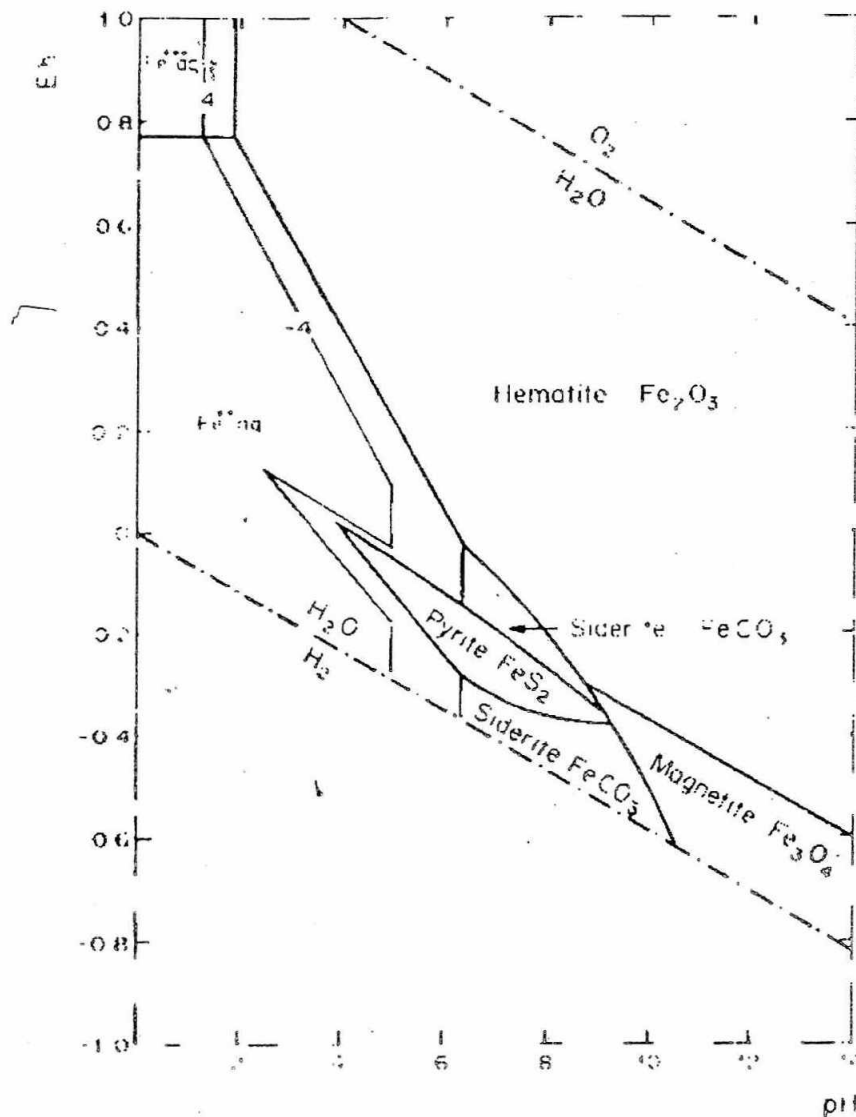


Fig.- 5.1 : Eh-pH diagram showing the stabilizing phases of iron in the sedimentary geochemical environment/ corresponding geochemical facies.

1- Magmatic magnetitic Iron Ore: magnetitic iron ore with ilmenite associated with basaltic suite of rocks (e.g. gabbro, anorthosite, norite)

2- Sedimentary iron ore deposits:

(i) Iron stones: They are non-cherty, oolitic, poorly banded, and largely of Phanerozoic age

(ii) Iron formations: They are typically laminated with chert, generally non-oolitic, and largely (but not exclusively) of Precambrian age. Banded Iron Formation bear anomalously high content of iron and has several synonyms world-wide e.g., Itabirite

(Brazil), Banded Iron Stone (South Africa), Quartz banded ores (Sweden), banded hematite quartzite/banded magnetite quartzite (India), jaspilite (USA and Australia), taconite (USA)

(iii) Black band and clay band ore, diagenetic and post diagenetic deposits of siderite and found in coal measures and in some clays

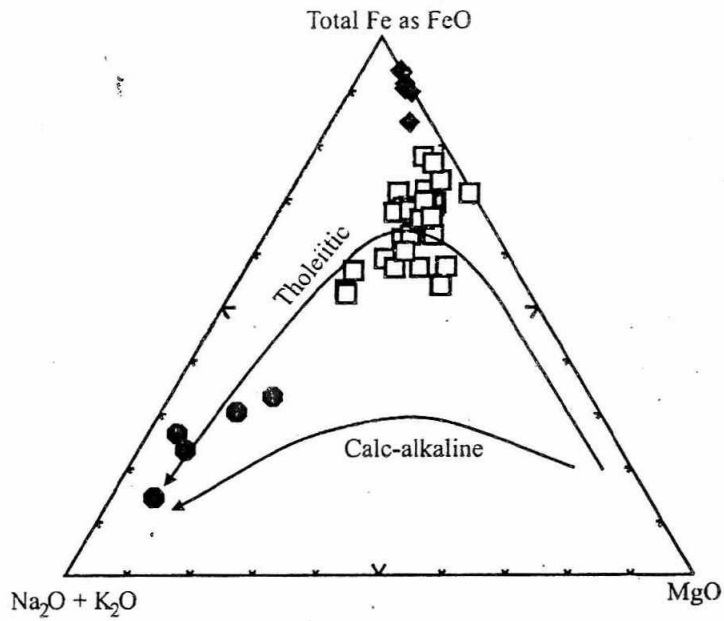
(iv) Bog iron ores found in many bogs and small lakes in higher altitudes

(v) Laterites derived by weathering of Fe-rich rocks

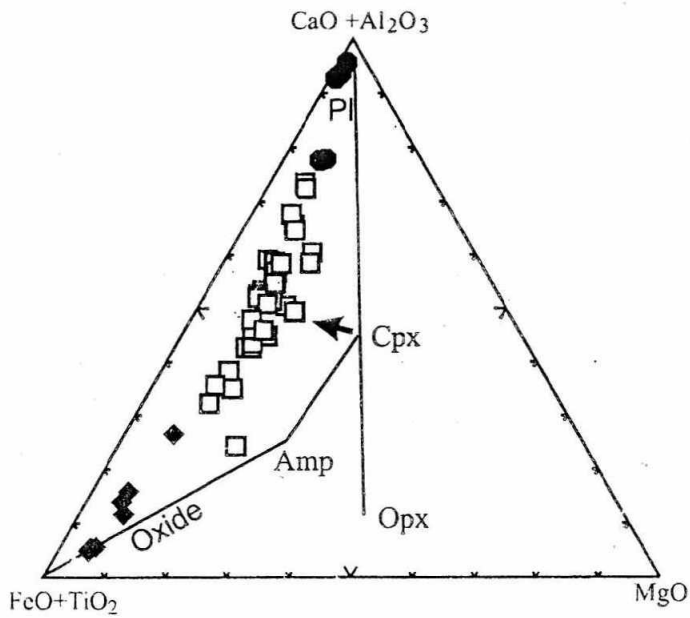
### GEOCHEMICAL SIGNATURE OF IRON ORES

Magmatic magnetitic iron ores are derived from Fe-rich evolved magma derived from the crystallization of basaltic melt (Fig.-2). These ores are associated with gabbro-anorthositic suite and hence are associated with plagioclase, clinopyroxene, orthopyroxene, olivine. Magnetite, martite are the main minerals with ilmenite and rutile as exsolution. The ore body used to contain the portion of gabbroic and anorthositic lamellae and spinel group of minerals. Hence, they contain significant amount of MgO, higher concentration of Ni, Zn, Cr, Co, anomalously high content of TiO<sub>2</sub> (sometimes ~14 wt% or higher), V<sub>2</sub>O<sub>5</sub> (sometimes upto about 2 wt%). They often host REE pattern of the ore is comparable to an evolved basaltic melt and positive Eu anomaly (Fig.-3). They also contain apatite as trace phase as a co-crystallising phase (Fig-4) due to which P-content increases. Some of the magnetitic ores are reported to contain platinum group of elements, Ge and monazite apatite etc. Some of them are also rich with zinc, which has a deleterious effect on extractive metallurgical process.

Iron formation facies are of oxide type, silicate type, carbonate type and sulphide type depending upon the thermodynamics (Fig.-1) of the depositional environment. The mineralogical association in these facies is given in the Table-1&2. It is to note that the dominant mineralogy of iron bearing phase differs (Hematite, magnetite, siderite, pyrite) and also their lithological attributes and host rock (Chert, quartzite, jasper, dolomite, argillite/shale, tuff). The shale/tuff in these deposits are very often found altered to gibbsitic-kaolinitic-litho unit. The iron ore associated with dolomitic itabirite used to have high LOI (as carbonate) and CaO, very low amount of silica and alumina whereas those associated with BHJ/BHQ contain higher amount of silica and alumina. BHJ/BHQ used to contain silica as high as 45-65 wt%. The ore often contains higher amount of alumina due to the association of kaolinite, gibbsite interlocked within associated goethitic matrix. They contain very low amount of the trace elements as observable from Table-3.



**A**



**B**

Fig.-5.2 : Geochemical variation in for a magmatic magnetitic iron ore (◆) and associated gabbro (□) and anorthosite (●). [A] AFM Diagram, [B] (CaO+Al<sub>2</sub>O<sub>3</sub>)-(FeO<sub>total</sub> + TiO<sub>2</sub>)-MgO plot, Pl= plagioclase, Amp= Amphibole. Opx= orthopyroxene, Cpx= clinopyroxene.

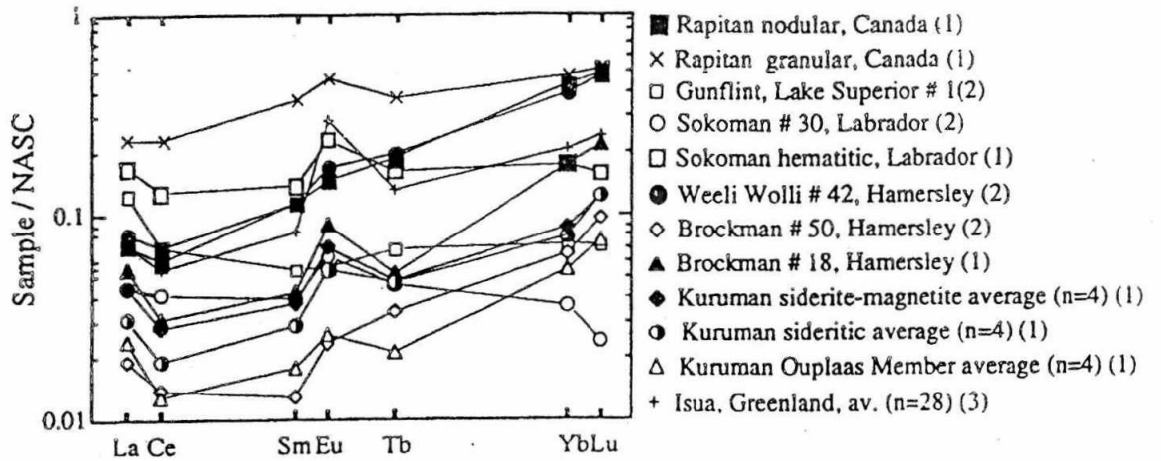
*Table-5.1 : Principal features of iron formation facies. Common but non-essential minerals in parentheses (after Mishra, 2000) .*

Facies	Iron minerals	Fe (wt%)	Lithology
<b>OXIDE</b>			
Hematitic	Hematite (magnetite)	30-40	Thin bedded to wavy bedded; alternate layers of bluish black hematite and grey or reddish chert (quartzite/jasper)
Magnetitic	Magnetite (minnesotaite, stilpnomelane, greenalite, siderite)	25-35	Evenly bedded to irregularly bedded; layers of magnetite alternate with dark chert and mixtures of silicates and siderite
<b>SILICATE</b>	Minnesotaite, stilpnomelane (magnetite, siderite greenalite, chamosite, chlorite)	20-30	Light to dark green rock of Fe-silicate minerals; generally laminated or evenly bedded, but may be wavy to irregularly bedded; commonly interlayered with magnetite oxide facies or carbonate facies, much of the chert is interstitial rather than in discrete layers
<b>CARBONATE</b>	Siderite (stilpnomelane, minnesotaite, magnetite, pyrite)	20-30	Evenly bedded or laminated alternation of siderite and chert
<b>SULPHIDE</b>	Pyrite, (siderite, greenalite)	15-25	Laminated to thinly layered carbonaceous argillite; rare chert

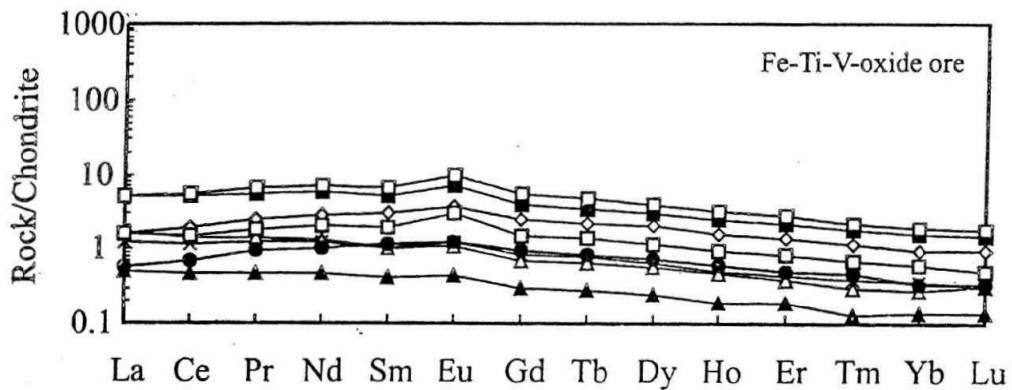
The REE pattern of the ore and the BIF is of marine sedimentary attributes with negative Ce anomaly, and are associated with positive Eu-anomaly (Fig-5.3). The REE pattern of BIF from Noamundi and Goromahisani (Bhattacharya, 2007) are presented for comparison (Fig.-5.5). Limited geochemical data on the BIF hosted iron ore indicate very low amount, in few tens of ppm, of trace elements. But there is a variation in the silica alumina content because of their mineralogical association and the mineral chemistry. Some of the possible association of minerals and their chemistry is listed in Table-5.1&5.2. Note that the Fe-bearing silicates also contribute high silica and alumina. The altered ores and secondary goethites contain clay minerals (kaolinite, gibbsite etc.) as enclaved pockets or as fracture fillings. The latter contribute to the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

TABLE-5.2. Iron-formation minerals, their compositions, and approximate compositional ranges in diagenetic to very low grade metamorphic assemblages

Mineral name	Simplified composition	Approximate compositional range
Chert (or quartz)	SiO <sub>2</sub>	none
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	none
Hematite	Fe <sub>2</sub> O <sub>3</sub>	none
Pyrite	FeS <sub>2</sub>	none
Greenalite	Fe <sub>6</sub> <sup>2+</sup> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub> *	(Fe <sub>4.0</sub> Mg <sub>1.0</sub> to Fe <sub>5.3</sub> Mg <sub>0.2</sub> ) Al <sub>0.0-0.2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub>
Stilpnomelane	(Fe, Mg, Al) <sub>2.7</sub> (Si, Al) <sub>4</sub> (O, OH) <sub>12</sub> ·xH <sub>2</sub> O with traces of K, Na, Ca	(Fe <sub>1.3</sub> Mg <sub>1.5</sub> Al <sub>0.1</sub> ) (Si <sub>3.7</sub> Al <sub>0.3</sub> ) to (Fe <sub>2.5</sub> Mg <sub>0.2</sub> ) (Si <sub>3.6</sub> Al <sub>0.3</sub> ) with K ≈ 0.1 to 0.2 and Na ≈ 0.05 per formula unit
Minnesotaite	Fe <sub>3</sub> <sup>2+</sup> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> *	Mg <sub>1.7</sub> Fe <sub>1.3</sub> to Fe <sub>2.8</sub> Mg <sub>0.2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>
Chamosite	(Fe <sup>2+</sup> , Al) <sub>6</sub> (Si, Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub>	(Fe <sub>3.3</sub> Mg <sub>1.3</sub> Al <sub>1.3</sub> ) (Si <sub>3.0</sub> Al <sub>1.0</sub> ) to (Fe <sub>3.8</sub> Mg <sub>1.3</sub> Al <sub>0.9</sub> ) (Si <sub>2.8</sub> Al <sub>1.2</sub> )O <sub>10</sub> (OH) <sub>8</sub>
Ripidolite	(Fe <sup>2+</sup> , Mg, Al) <sub>12</sub> (Si, Al) <sub>8</sub> O <sub>20</sub> (OH) <sub>16</sub>	Composition in iron-formation: (Fe <sub>5.5</sub> Mg <sub>4.3</sub> Al <sub>2.3</sub> ) (Si <sub>5.4</sub> Al <sub>2.6</sub> )O <sub>20</sub> (OH) <sub>16</sub>
Riebeckite	Na <sub>2</sub> (Fe <sup>2+</sup> , Mg) <sub>3</sub> Fe <sub>2</sub> <sup>3+</sup> Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>	Fe <sup>2+</sup> /(Fe <sup>2+</sup> +Mg) ranges from 0.64 to 0.86
Ferri-annite	K <sub>2</sub> (Mg, Fe) <sub>6</sub> Fe <sub>2</sub> <sup>3+</sup> Si <sub>6</sub> O <sub>22</sub> (OH) <sub>4</sub>	Fe <sup>2+</sup> /(Fe <sup>2+</sup> +Mg) ranges from 0.50 to 0.71
Siderite	FeCO <sub>3</sub>	(Mg <sub>0.3</sub> Mn <sub>0.1</sub> Fe <sub>0.6</sub> ) to (Mg <sub>0.2</sub> Mn <sub>0.2</sub> Fe <sub>0.6</sub> ) CO <sub>3</sub>
Dolomite-ankerite	CaMg ↔ CaFe(CO <sub>3</sub> ) <sub>2</sub>	Ca <sub>1.0</sub> (Mg <sub>0.8</sub> Fe <sub>0.1</sub> Mn <sub>0.1</sub> ) to Ca <sub>1.0</sub> (Mg <sub>0.5</sub> Fe <sub>0.2</sub> Mn <sub>0.3</sub> ) to Ca <sub>1.0</sub> (Mg <sub>0.4</sub> Fe <sub>0.6</sub> ) (CO <sub>3</sub> ) <sub>2</sub>
Calcite	CaCO <sub>3</sub>	Ca <sub>0.9</sub> (Fe, Mg, Mn) <sub>0.1</sub> CO <sub>3</sub>

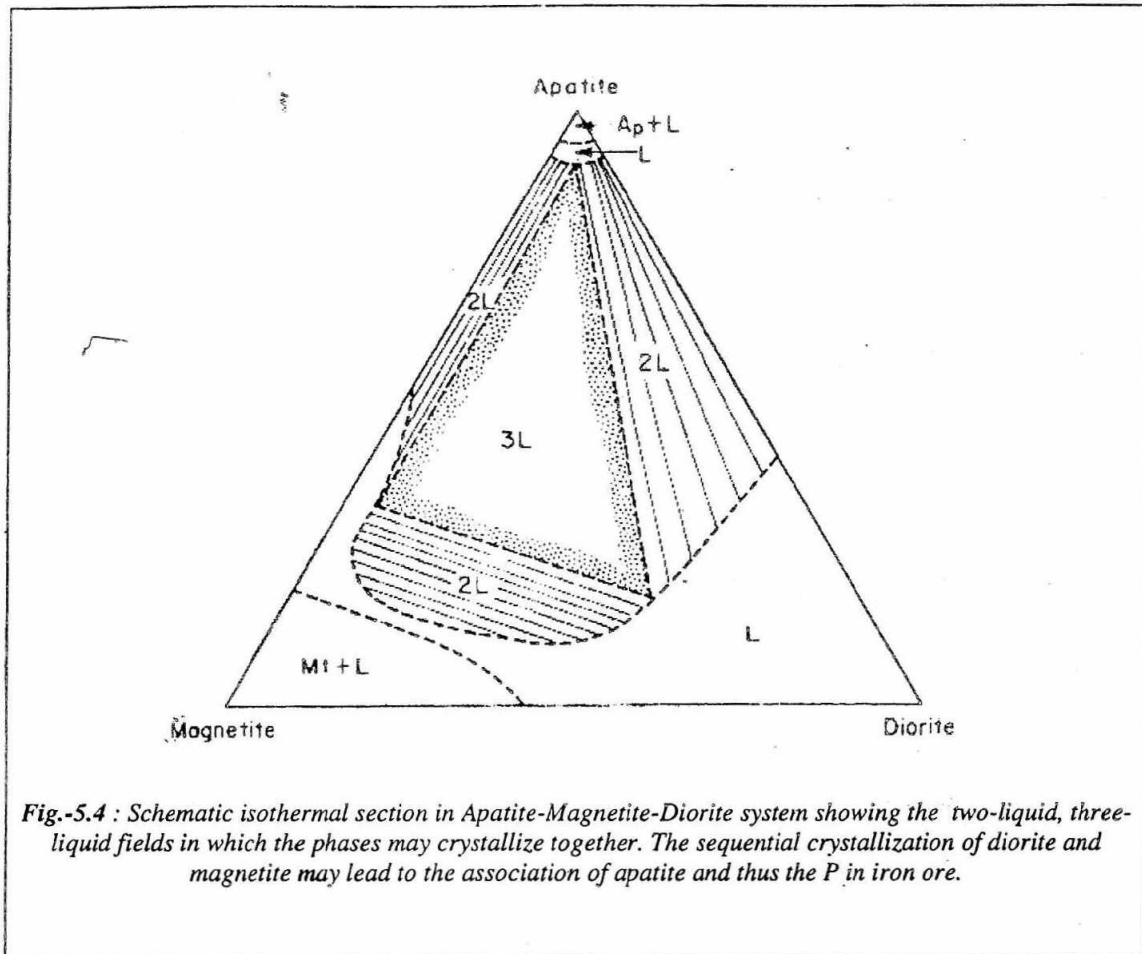


[A]



[B]

**Fig-5.3 :** REE geochemistry of iron ores. [A] North American shale composite normalized REE pattern of selected Archean Proterozoic iron formations with broadly negative Ce-anomaly and positive Eu anomaly. [B] Chondrite normalized REE pattern of magmatic magnetitic iron ore.



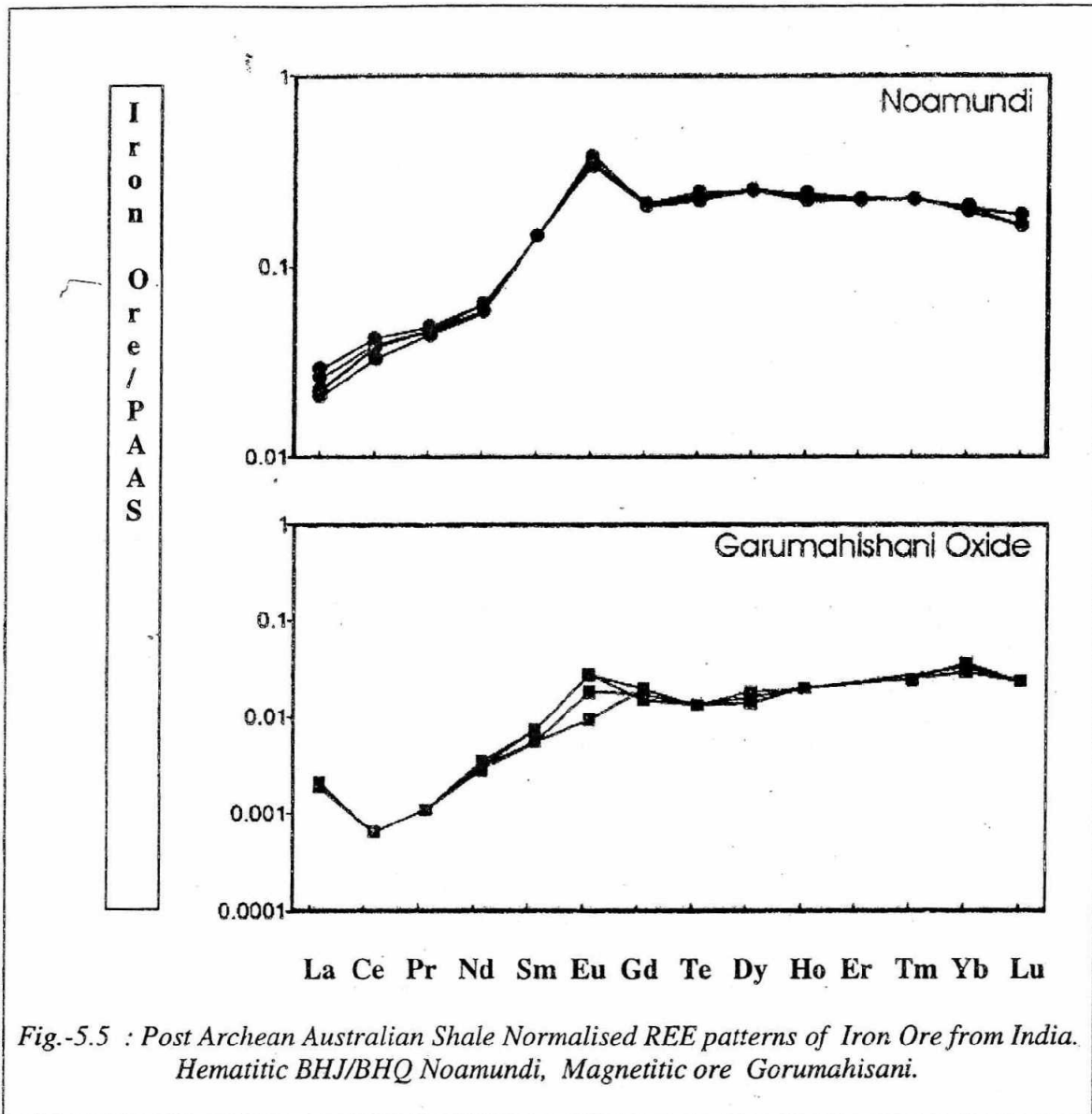
## MINERAL CHEMISTRY OF IRON ORES

Hematite, magnetite, martite are the major iron bearing minerals in the iron ore. Secondary goethite is also an intricately associated major phase. The ores of magmatic types are often associated with ulvospinel and ilmenite as exsolution lamellae (Fig.-6E), and rutile as alteration product within magnetite. Magnetites may contain Ti, Zn, V in its lattice which is reflected in the ore geochemistry (Table-5.3). The chemistry of magnetite-ilmenite is given in Table-5.4. They are also associated with trace amount of sulphides such as pyrrhotite (Fig.-5.6 C,D,F) and phosphates such as apatite  $[\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})]$ , monazite contributing to P and S to the bulk chemistry. The associated gangue components are Fe-bearing silicates such as chlorite, tremolite, serpentine, talc and dolomites the chemistry of which is given in Table-5.5. These silicates contribute to high  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  in the ore. In comparison, hematite is free from most of the trace elements (Table-5.4). The BIF hosted supergene enriched iron ore as found in Sighbhum- north Orissa contain dense martite, microplaty hematite, vitreous goethite, ochreous goethite as their ore minerals. They are associated with chert, altered shale and tuff and kaolinitic fracture fillings.



Table-5.3 : Geochemical data of Iron ores from different sources Iron formation (1-9) and magmatic magnetitic ore (10). (after Spier et al, 2007; Bhattacharya et al, 2007; Mohapatra et al, 1987; Zhou et al., 2007)

	Itabirite	Itabirite	Itabirite Iron ore	BIF Noamu- ndi	BIF Noam- undi	Barsua Iron Ore	Barsua Blue dust	Goru- mahisa ni BIF	Gorum- ahisani BIF	Magn itic or
	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub>	1.01	41.74	0.91	62.71	62.74	18.20	0.60	45.85	44.87	4.56
TiO <sub>2</sub>	0.02	<0.01	<0.01	0.03	0.02	0.16	0.38	0.00	0.00	15.3
Al <sub>2</sub> O <sub>3</sub>	0.32	0.18	0.28	0.38	0.35	0.75	0.42	0.04	0.12	4.86
Fe <sub>2</sub> O <sub>3</sub>	48.90	55.71	77.88	36.79	36.69	79.23	97.84	50.42	51.69	72.3
FeO	0.66	0.71	0.32							
MnO	0.28	<0.01	0.12	0.00	0.00			0.84	0.73	0.38
MgO	10.33	0.14	4.11	0.08	0.08			1.80	1.34	5.52
CaO	14.36	0.46	5.45	0.00	0.00			0.90	1.13	0.87
Na <sub>2</sub> O	<0.01	<0.01	<0.01	0.00	0.00			0.00	0.00	0.06
K <sub>2</sub> O	0.03	<0.01	0.02	0.00	0.00			0.08	0.08	0.02
P <sub>2</sub> O <sub>5</sub>	0.12	0.13	0.12	0.08	0.12			0.08	0.08	0.00
LOI	22.77	0.59	9.91				0.20			0.00
Total				100.07	100.0			100.0	100.04	99.19
S			<0.01		0			1		1.01
Ti				490	342			7	3	
V			36.3	15	34			1	1	4524
Cr				0.5	1			1	0	950
Mn				53	92	25	40	275	980	
Co				1	1	93	120	9	25	257
Ni			15.1	5	5	32	50	16	104	214
Cu			<1.0	0.9	0.4	27	31	1	48	404
Zn			12.9	2.5	5	150	57	14	416	474
Ge			3.6	47	53			43	30	
As				12	13			2	4	
Ba			11.2	7	8					6.5
La				1.09	0.78			0.08	0.07	0.46
Ce				3.37	2.61			0.05	0.05	1.11
Pr				0.43	0.39			0.01	0.01	0.17
Nd				2.06	1.84			0.09	0.1	0.88
Sm				0.81	0.83			BDL	0.04	0.24
Eu				0.37	0.42			0.03	0.03	0.11
Gd				0.97	0.99			0.09	0.09	0.25
Tb				0.17	0.19			0.01	0.01	0.04
Dy				1.13	1.09			0.07	0.06	0.25
Ho				0.24	0.22			0.02	0.02	0.04
Er				0.66	0.64					0.11
Tm				0.09	0.09					0.01
Yb				0.57	0.54			0.09	0.08	0.01



### SIGNIFICANCE TO MINERAL PROCESSING

From the above discussion, it is to note that the chemical contribution of gangue component to the ore is easy to comprehend if the lithology, mineralogy and mineral chemistry is known.  $\text{SiO}_2$  is contributed not only by chert or quartz but also by silicate minerals like pyroxene and even by kaolinitic clay.  $\text{Al}_2\text{O}_3$  may be contributed by gibbsite, kaolinite [ $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ] and some silicate minerals (e.g., chlorite) as well. In a mining process, the lean grade ore (BIF) and associated bedded rocks, overburden material get mixed up with the ore and contribute to higher gangue component to be processed by beneficiation. As the demand of iron ore is increasing, the lean grade ores also find

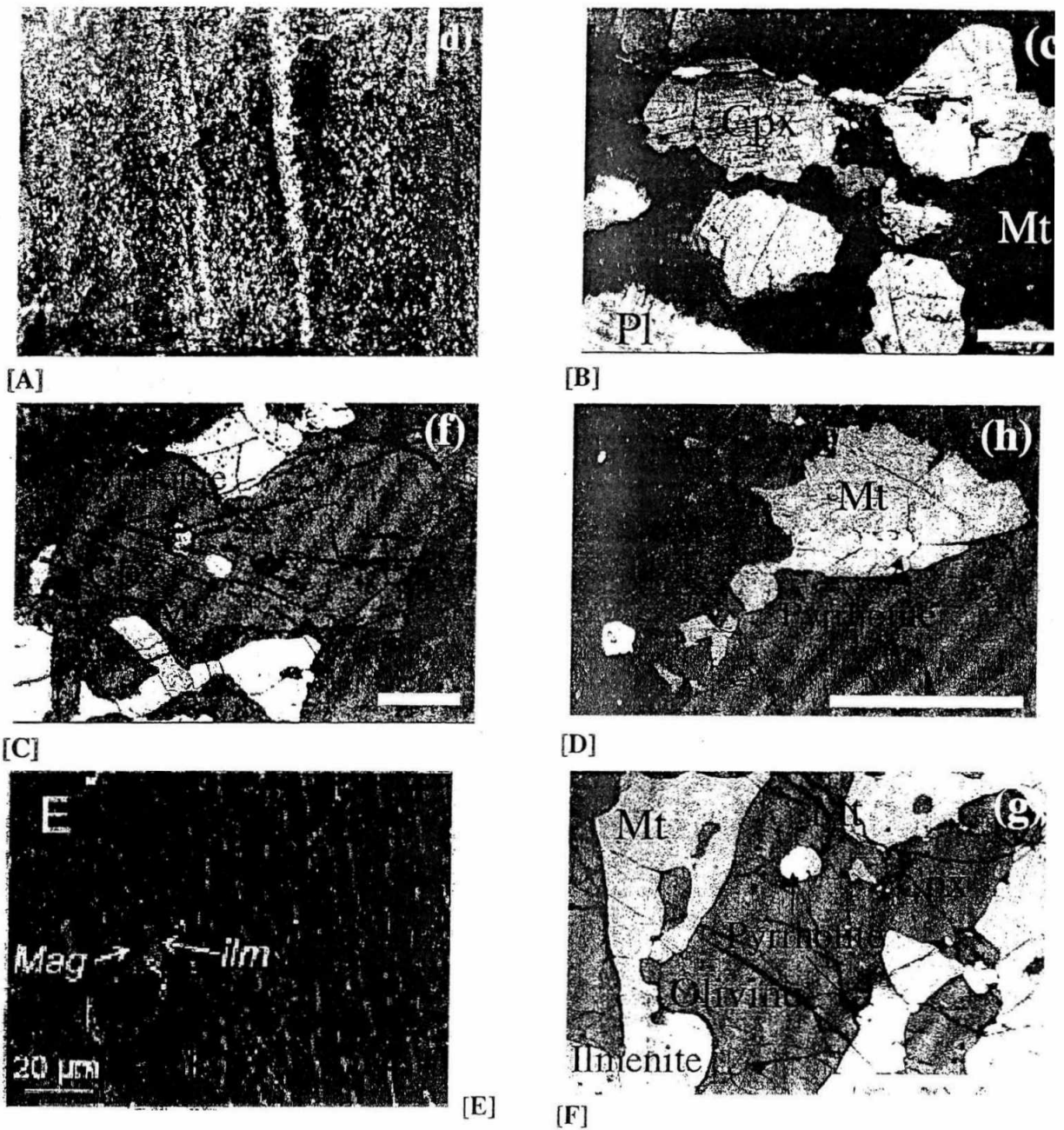


Fig.-5.6 : Ore and gangue in magmatic magnetitic iron ore. The mineralogical varieties and abundance controls the chemistry of the ore. [A]- Megascopic sample, [B-F] Magnetitic iron ore under optical microscope. Mt, Mag= magnetite, ilm= ilmenite Cpx= clinopyroxene, Am= amphibole, Pl= plagioclase.

Table-5.4: Mineral chemistry of major iron bearing minerals in iron ore (EPMA Data is from McEnroe et al., 2001; Harlov et al., 2002; Saha, 1994).

	Magnetite Bakka Norite	Magnetite	Ilmenite Sokndal	Hematite	Magnetite Kumhardubi	Ilmenite Kumhardubi
SiO <sub>2</sub>	0.142	0.004	0.010	0.04		
TiO <sub>2</sub>	4.108	0.145	48.692	0.95	10.26	25.72
Al <sub>2</sub> O <sub>3</sub>	0.00	0.187	0.000	0.03	3.75	1.63
Cr <sub>2</sub> O <sub>3</sub>	0.068	1.374	0.062	0.03		
V <sub>2</sub> O <sub>3</sub>	0.328	0.644	0.229		1.18 (V <sub>2</sub> O <sub>5</sub> )	1.31 (V <sub>2</sub> O <sub>5</sub> )
Fe <sub>2</sub> O <sub>3</sub>	59.964	65.755	10.765	93.3		
FeO	33.855	30.51	35.381	ND	80.85	67.85
MgO	0.00	0.208	4.531	ND	0.40	0.19
CaO	0.081	0.000	0.004	ND		
MnO	0.225	0.000	0.334	ND	0.12	0.12
ZnO	0.804	0.082	0.000	ND		
Total	99.575	100.299				

Table-5.5 : Mineral chemistry of minor iron bearing minerals in iron ore (EPMA Data is from Harlov et al., 2002).

	Talc	Chlorite	Serpentine	Dolomite	Tremolite	Muscovite
SiO <sub>2</sub>	62.1	33.0	45.8	0.02	56.6	50.7
TiO <sub>2</sub>	0.02		ND	0.01	0.01	0.46
Al <sub>2</sub> O <sub>3</sub>	0.57	16.4	0.51	ND	1.04	28.4
Cr <sub>2</sub> O <sub>3</sub>	0.03	0.01	0.01	0.01	ND	0.02
V <sub>2</sub> O <sub>3</sub>						
Fe <sub>2</sub> O <sub>3</sub>						
FeO	2.06	5.63	1.64	0.79	4.21	5.20
MgO	30.5	32.4	41.0	22.0	22.8	2.36
CaO	0.04	0.05	0.11	34.3	11.6	0.12
MnO	ND	0.09	0.13	0.50	0.05	ND
Na <sub>2</sub> O	0.03	0.01	ND	ND	1.35	0.11
K <sub>2</sub> O	0.01	0.01	ND	ND	0.39	9.96
F	0.18		0.81	ND	0.56	ND
Cl	0.01		0.03	0.02	0.02	0.01
Total	95.5	87.6	90.0	57.6	98.4	97.4

application for mineral processing. So, the idea on geochemistry and mineral chemistry may be of future interest to mining engineers and mineral engineers.

The geochemical database on different litho units in mines, their mineralogy may help to decipher the possible utility for various industrial products. Suitable mining plan for excavation can be designed to achieve ore, BIF, altered shale by their classification as market-products at the site itself. If other values are found, a suitable mineral processing can be planned. It will help in the lowering of waste and environmental damage and efficient resource utilization.

Magnetite-ilmenite-ulvospinel type ore is of interest for the recovery of Ti and V. But the textural association as few-micron thick exsolution lamellae (Fig.-6E) is a cause of interlocking. Critical research is required for the mineral processing for this type of ores.

It may be noted that earth's resource is limited. Most of the iron ore deposits are of Precambrian time (about 2500 million years old). So, optimization of iron ore utility, even of lean grade should be of top priority today so that the life of the mines can be enhanced. It requires research for the recovery of minerals from the lean grade ores (say BFQ/BHJ) or their utilization.

## CONCLUSION

The geochemistry of ore and associated litho units and mineral chemistry gives conclusive information on the metal and trace metal distribution patterns. It assists in decision making on the gangue component and its recovery possibility. It may also help in decision making of suitable technological approach to recover trace but rare metals present in the ore either by mineral processing or by metallurgical process. As the Technology is heading towards lean grade ores, resource conservation and environment friendliness, geochemical and mineral-chemical understanding of iron ores may be of great interest in future.

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