

*CHAPTER 6*

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**HYDROTHERMAL ALTERATION**

# **HYDROTHERMAL ALTERATION OF QUARTZITES AND PEGMATITES**

## **6.1 INTRODUCTION**

The geology of Delhi region includes pockets of clay deposits surrounded by extensive zones of friable to loose sand deposits. These are mainly used in ceramic, building and other industrial purposes. The altered products of Delhi quartzites include pockets of variegated, loose to moderately packed sand located within quartzite ridge. The pegmatites has nearly totally transformed to give rise kaolinite deposits. These china clay (kaolinite) deposits occur within the highly weathered zones of quartzites. The clay may represent the residual deposits derived from alteration of feldspars of pegmatites (Tyagi, 1980). Srivastava et al. (1974) noted that pegmatites, in general, traversing the country rock have shown little thermal contact affects. At the pegmatite quartzite contact zone, massive quartzite have become friable with the development of secondary feldspar within the interlocking fabric of quartzite, besides minor amount of muscovite and tourmaline. The accompanying quartz veins do not show any contact effect with the host rock. The above observation indicates that the alteration of feldspar in the pegmatites to kaolinite and the complete destruction of interlocking texture of quartzite were probably brought about by the late hydrothermal activity associated with pegmatite intrusion in the area (Rakesh Kumar, 1989) and later weathering and/or alteration processes.

Most of the specialised literature indicates that hydrothermal alteration has affected many rock types (Rose and Burt, 1979). The principle objective behind their studies were to see whether there has been any relationship with these hydrothermal alteration to ore formation. However there are very few hydrothermal ore deposit that lack associated wall rock alteration, but there are many areas of hydrothermal alteration that are essentially barren of ore deposits (Burnham, 1962).

The extent of hydrothermal alteration and the formation of dispersion haloes are partially dependant upon the structural and compositional properties of the wall rocks and the solution passing through them. Hydrothermal alteration occurs within a wide range of physicochemical conditions. Hydrothermal alteration is defined as the interaction of rocks with hot waters. Hydrothermal solution refers to all types of hot water that exist in the earth crust. The temperature is appreciably warmer (e.g. 5 °C or more) than the wall rock. Weathering is a low temperature near surface process acting commonly from top to bottom, and the temperature of solution responsible for the weathering may only be slightly different from that of the rock.

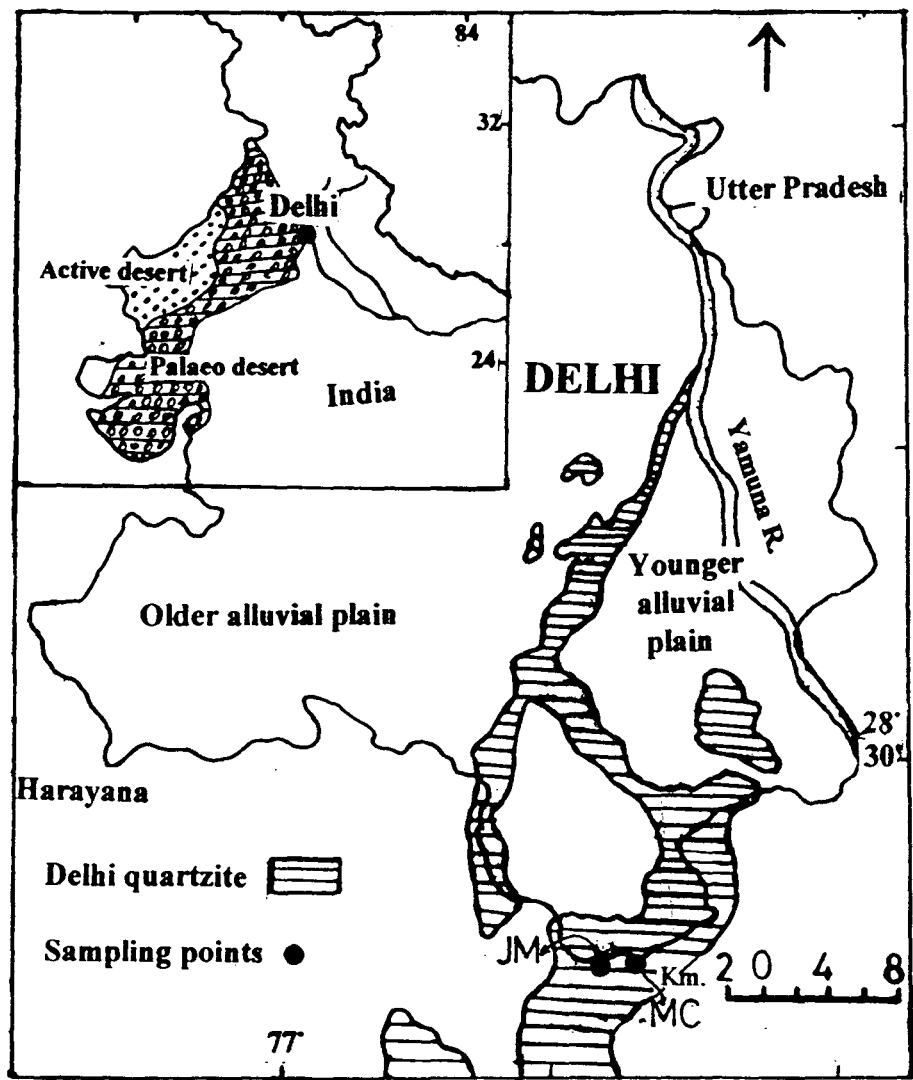
The purpose of the present study is to evaluate the process of formation of clay and sand deposits from the protolith using geochemical and mineralogical data. Development of alteration haloes around pegmatite and their alteration/weathering have important significance to the behaviour of nuclear waste in the geological environment. Particularly the behaviour of REE in aqueous solution may be used as analogue for the behaviour of elements of actinide series (Wood, 1990; Rard, 1988).

## **6.2 FIELD OBSERVATION AND SAMPLING**

Numerous pegmatite intrusions are seen in the Delhi ridge area. The pegmatites and surrounding aureoles of altered quartzites were transformed to china clay and loose sands, respectively. These sands vary in colour from red, yellowish to white followed by kaolinite pockets both laterally inside and vertically downward. The two sampling locations have different local geology on the basis of overlying sediments. A thick profile of transported sediments found to occur on the Mohabtabad weathered quartzites (Figure-6.1), whereas, the Mohabtabad Chouki sampling site lacks the deposition of transported sediments. Generally the altered pegmatites comprise mainly of clay pockets in which big quartz grains, muscovite flakes and tourmaline grains also occur.

Rakesh Kumar (1989) has observed that the pegmatite dykes run parallel to the strike of the quartzite ridges trending NE-SW to NW-SE. Srivastava et al. (1974) reported that the pegmatites of South Delhi area have intruded along the joints which cut through the quartzites in all directions as well as along shear zones running parallel to the strike of the formations and also oblique to it.

The samples were taken on colour basis. Sands of ferruginous (red), yellowish and white colour and kaolinite have been sampled and processed for their geochemical and mineralogical study (Plate 2.1d and 2.2 c&d). Nearly 4 kg of each samples were homogenised and 1 kg of each have been separated to make it to -60 mesh. The 200 gm of each 60 mesh sample have been made to -200 mesh. Fresh quartzite samples (JM9 and JM10) were also taken nearly 50 meters away from the alteration zones (see Chapter- 3). The visual characteristics of samples is shown in Table 6.1.



**Figure 6.1: Geological map of Delhi area showing sampling locations of altered pegmatites and quartzites.**

**Table-6.1****Mohabtabad**

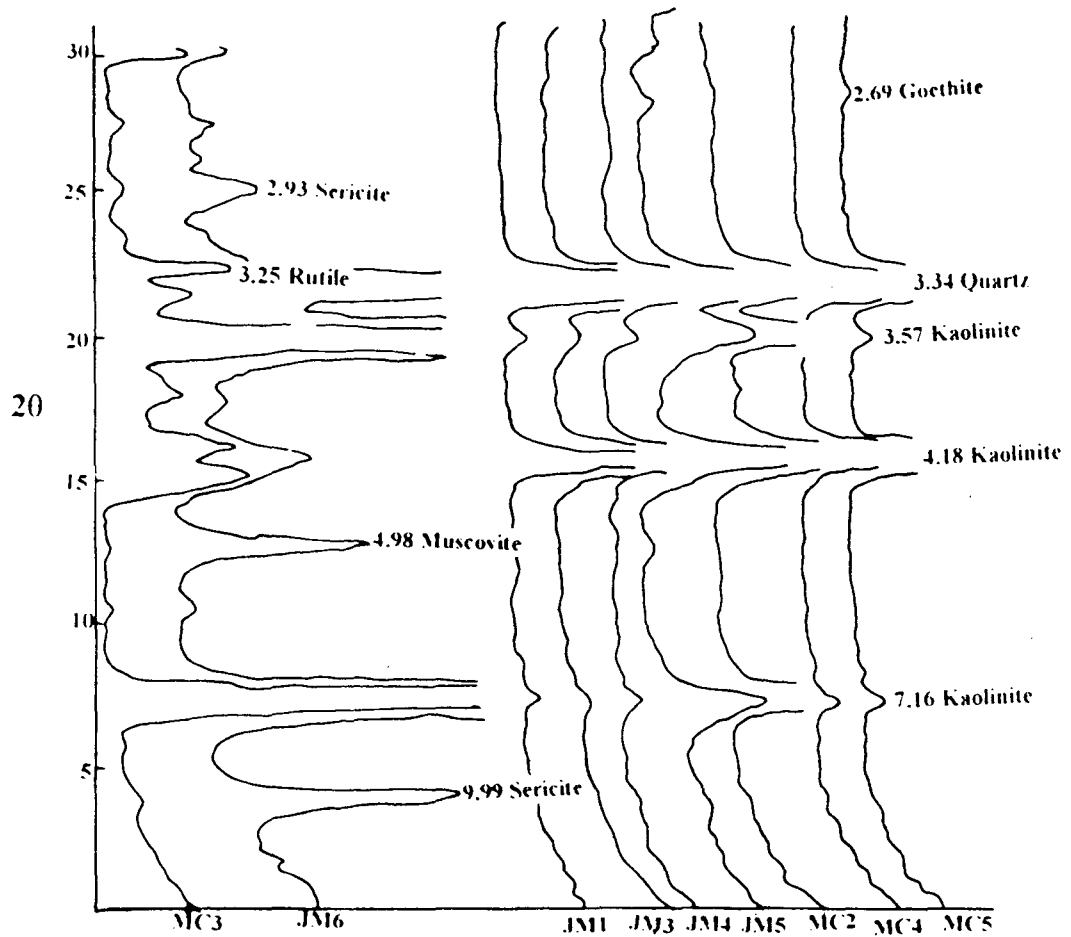
<b>Sample</b>	<b>Colour</b>	<b>Variety</b>
JM6/5	Brownish red	Ferruginous sand-medium grained
JM5/4	Yellow	Ferruginous sand-medium grained
JM4/3	Red	Ferruginous sand-medium grained
JM3/2	White	Silica sand - medium grained
JM2/1	White	Silica sand - Coarse grained
JM1/6	Whitish	Clay-fine grained

**Mohabtabad Chouki**

MC5/4	Red	Ferruginous sand-medium grained
MC4/3	White	Silica sand-medium grained
MC3/2	White	Clay-fine grained
MC2/1	White	Silica sand-medium grained

**6.3 RESULTS****6.3.1 Mineralogy**

Mineralogy of the altered pegmatites has been studied by using XRD (see Figure- 6.2) and also IR techniques (Figure. 6.3) of some the samples. The samples are mainly



**Figure 6.2: X-ray diffractogram of hydrothermally altered samples of pegmatites. d values (Å) are shown with the mineral names.**

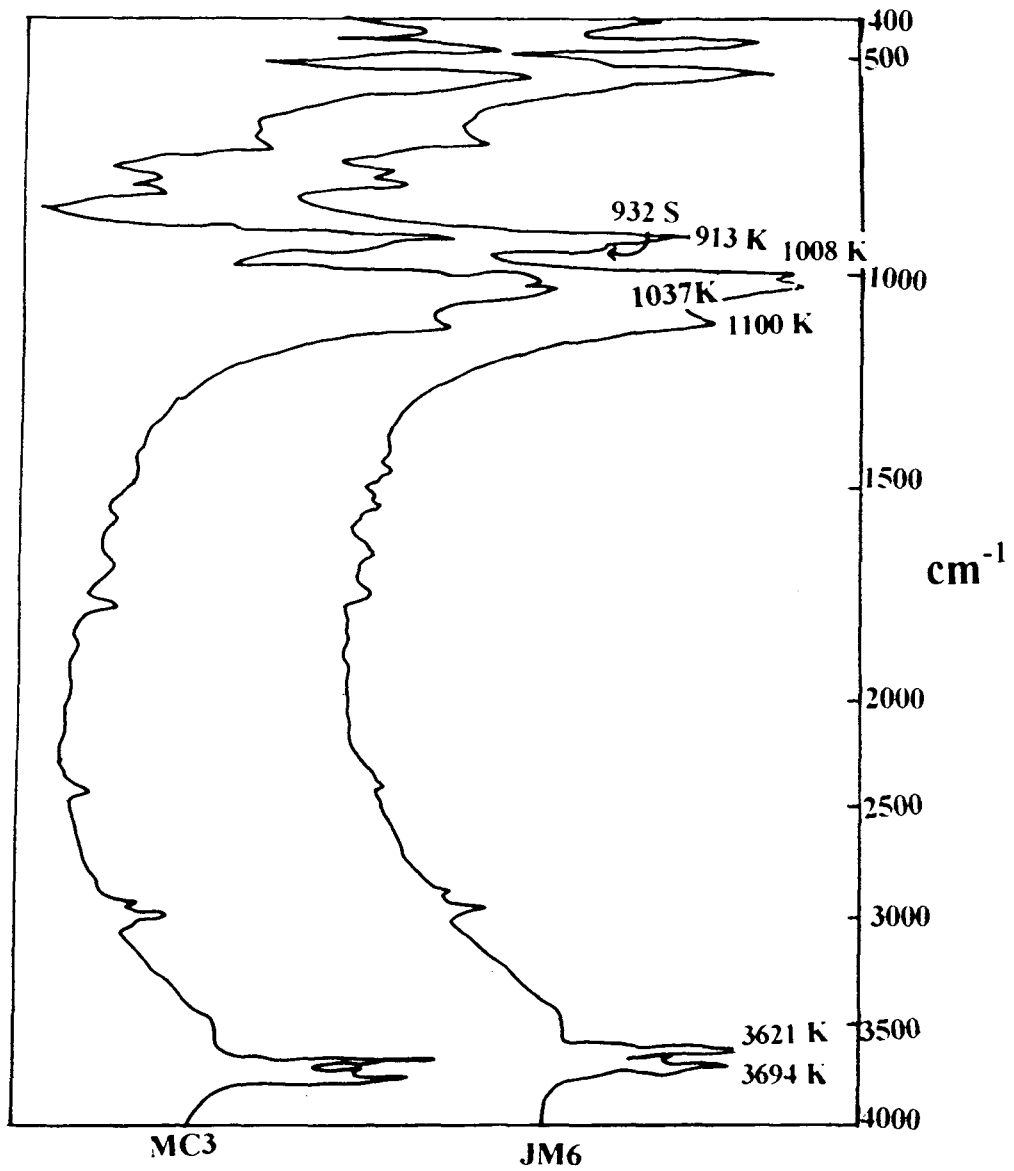


Figure 6.3: IR graph of clay rich altered samples, K and S represent kaolinite and sericite respectively.



composed of kaolinite ( $7.16 \text{ \AA}^\circ$ ) and quartz ( $3.34 \text{ \AA}^\circ$ ). Small amount of sericite ( $d=16.1 \text{ \AA}^\circ / 9.6 \text{ \AA}^\circ / 4.92 \text{ \AA}^\circ / 2.93 \text{ \AA}^\circ$ ) are also found in JM6/1. The silica sand which is white in colour (JM1/2) composed mainly of quartz and small amount of kaolinite. The morrum sands (JM5/6) are made up of quartz and trace amount of kaolinite. Secondary peak of goethite ( $2.68 \text{ \AA}^\circ$ ) are also encountered in JM5/6 and MC5/4 but the primary peaks of goethite may have been overlapped by kaolinite peak ( $4.18 \text{ \AA}^\circ$ ).

The XRD analysis were also confirmed by IR analysis. In IR spectrum the kaolinite troughs and a trough characteristic of sericite ( $932 \text{ cm}^{-1}$ ) were encountered in the JM6/1 (Figure-6.3).

Rutile is encountered in MC3/2 ( $3.25 \text{ \AA}^\circ$ ). The  $\text{TiO}_2$  content of JM6/1 also warrants the presence of rutile which could have been masked by pronounced broad quartz peak ( $3.3 \text{ \AA}^\circ$ ) in the X-ray diffractogram.

Relative abundance of various minerals are shown in the following Table-6.2.

**Table-6.2**

Sample	Quartz	Kaolinite	Sericite	Goethite	Rutile
JM6 /1	23.7	48.0	28.3		
JM1/2	99	1			
JM3/4/	92.3	7.7			
JM4/5	99.6	0.4			
JM5/6	83.3	15.6		1.2	
MC2/1	81	19			
MC3/2	1.2	97.2			1.6
MC4/3	98.6	1.36			
MC5/4	98.7	1.1		0.2	

### **6.3.2 Major and trace elements geochemistry**

Geochemical composition of the weathered products of the pegmatites and quartzites is shown in Table- 6.3. Crystallochemical nature of the elements and mineralogical results have been used to understand correlation data of analyses of the samples. Inter-element correlation matrix is shown in Table- 6.4.

The high silica content and negative correlations with other elements/oxides, may be due to the occurrence of free silica as quartz, and it also suggests that the quartz has dilution effects on other elements.

The correlation between LOI and  $\text{Al}_2\text{O}_3$  is because of the clay content, which can absorb water. From the mineralogical study it is evident that the Al mainly comes from kaolinite and in JM6/1, it is also from sericite. Although, good correlation of Al and Ti suggests a substitution for Al by Ti, but very good correlation among Ti, P, Zr, Y and Ba could be attributed to the concentration of HFSE minerals, like rutile, apatite, zircon and their altered products like florencite after apatite.

Since Ti does not correlate with Fe, the probable Ti mineral would be  $\text{TiO}_2$  mineral (rutile).  $\text{P}_2\text{O}_5$  has a good correlation with CaO, which can be due to the presence of apatite. High Zr contents in some of the samples suggest presence of high amount of zircon, but where it is low, could be attributed to the dilution effects of other minerals (quartz and kaolinite).

The good correlation between Ca and Mg may be due to the similar geochemical behaviour of these elements. The same reason can be given to the good correlation of K and Ba.

**Table 6.3: Major and Trace element chemistry of alteration products (sand and clay)**

	JM6/1	JM1/2	JM2/3	JM3/4	JM4/5	JM5/6	MC2/1	MC3/2	MC4/3	MC5/4
SiO <sub>2</sub>	50.3	99.2	90.6	96.4	97.5	90.4	89.4	48.7	96.5	97.2
TiO <sub>2</sub>	3.61	0.09	0.12	0.17	0.07	0.24	0.85	4.71	0.07	0.08
Al <sub>2</sub> O <sub>3</sub>	29.9	1	7.2	0.99	0.71	4.23	5.65	35	0.5	0.57
FeO	0.88	0.11	0.11	0.24	0.24	1.3	0.15	0.33	0.1	0.28
MnO	0.007	0.002	0.002	0.001	0.002	0.004	0.003	0.003	0.001	0.001
MgO	0.23	0.01	0.02	0.02	0.03	0.11	0.05	0.11	0.04	0.04
CaO	0.26	0.02	0.02	0.02	0.02	0.1	0.02	0.04	0.02	0.02
Na <sub>2</sub> O	0.22	0.01	0.06	0.01	0.03	0.06	0.08	0.17	0.01	0.02
K <sub>2</sub> O	1	0.03	0.02	0.03	0.04	0.16	0.01	0.08	0.02	0.02
P <sub>2</sub> O <sub>5</sub>	0.24	0.02	0.04	0.02	0.02	0.05	0.02		0.01	0.01
LOI	10.8	0.44	2.77	0.51	0.38	2.35	2.24	10.3	0.38	0.38
Ba	486.6	4.47	10.81	16.34	8.88	53.27	12.4		4.69	5.5
Sr	1.96	6.22	16.52	16.62	9.27	46.18	14.7		7.6	7
Ni	17.95	8.45	22.2	11.7	7.8	26.95	5.55		4.45	4.65
Cr	74.5	31.3	40.55	43	41.3	65.5	20		12.9	15.55
Zr	420.1	55.15	78	63	66	114.5	232.5	99.43	42.15	57
Y	30.05	2.81	5.7	5.5	2.8	28.3	13.1		2.62	4.3
CIA	98.69	99.95	99.95	99.94	99.92	99.66	99.88	99.55	99.91	99.91

**Table 6.4: Correlation matrix for the chemistry of alteration products (sand and clays).**

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	LOI	Zr	Ni	Cr	Ba	Sr	Y
SiO <sub>2</sub>	1.00																
TiO <sub>2</sub>	-0.98	1.00															
Al <sub>2</sub> O <sub>3</sub>	-0.99	0.99	1.00														
FeO	-0.35	0.25	0.29	1.00													
MnO	-0.74	0.65	0.69	0.75	1.00												
MgO	-0.81	0.73	0.76	0.74	0.96	1.00											
CaO	-0.65	0.54	0.59	0.70	0.95	0.94	1.00										
Na <sub>2</sub> O	-0.97	0.92	0.95	0.43	0.85	0.87	0.76	1.00									
K <sub>2</sub> O	-0.67	0.56	0.61	0.57	0.91	0.91	0.98	0.77	1.00								
P <sub>2</sub> O <sub>5</sub>	-0.98	0.97	0.98	0.57	0.94	0.94	0.98	0.95	0.99	1.00							
LOI	-1.00	0.96	0.99	0.38	0.78	0.83	0.69	0.98	0.70	0.98	1.00						
Zr	-0.65	0.56	0.59	0.46	0.88	0.83	0.87	0.80	0.88	0.89	0.68	1.00					
Ni	-0.39	0.24	0.41	0.72	0.54	0.45	0.46	0.41	0.36	0.42	0.45	0.25	1.00				
Cr	-0.68	0.60	0.67	0.80	0.83	0.74	0.78	0.67	0.72	0.75	0.70	0.56	0.80	1.00			
Ba	-0.98	0.98	0.97	0.53	0.91	0.93	0.97	0.93	1.00	0.99	0.97	0.89	0.33	0.69	1.00		
Sr	0.19	-0.30	-0.22	0.63	0.10	0.04	-0.05	-0.13	-0.22	-0.18	-0.16	-0.17	0.67	0.36	-0.26	1.00	
Y	-0.77	0.71	0.73	0.90	0.92	0.90	0.85	0.79	0.75	0.77	0.78	0.77	0.66	0.79	0.73	0.44	1.00

Relatively intermediate correlation between Ti and Al may suggest occurrence of tourmaline, but Ti is not correlated with Na, Mg and Fe. Therefore it, also suggest for free TiO<sub>2</sub> minerals, i.e. rutile. The presence of rutile is indicated by XRD data.

The correlation between Fe, Mn, Cr and Ni are due to their similar geochemical behaviour and occurrence. Fe does not correlate with Mg, Ca, Al, and therefore discrete phases, like oxide or hydroxide must be present.

So, it can be predicted that quartz, kaolinite, HFSE minerals (rutile, zircon, apatite), oxide/hydroxide of Fe and Mn are the phases occur in the alteration zones in different proportions. Quartz has diluting effects on the concentrations of other elements.

From the mineralogical and geochemical results it is suggested that kaolinisation is the major process that has affected pegmatite minerals. The high CIA values also indicate kaolinisation and the formation of kaolinite at the expense of feldspar. Although kaolinisation is a dominant process, but in one of the altered pegmatite sample the sericitisation is also encountered (JM6/1). These sericitised samples also show relatively lower CIA.

The uppermost weathered quartzite of Mohabtabad seem to have gained sediment component from above. This is due to the transport of small grain size sediments to the porous weathered quartzite (Brimhall et al., 1991). The incorporation of overlying sediments is clearly reflected in the geochemical composition of JM5/6. Concentrations of all the elements present in the overlying sediments have gone up excepting SiO<sub>2</sub>, and there is a similarity in major and trace element composition with overlying sediments.

The CIA has been calculated after Nesbitt and Young (1984) (see Chapter-2). The samples show high CIA values (98.69 to 99.95) indicating intensive leaching of alkali elements. The lower CIA values of JM6/1 is due to the presence of sericite indicating less intense alteration weathering. The CIA values also confirm to the CIA (100) of Kaolinite.

### **6.3.3 REE chemistry**

The REE composition of weathered materials are shown in Table- 6.5. Chondrite normalised patterns are shown in Figure 6.5 and 6.6. All the samples show LREE enriched and nearly flat HREE patterns. The samples show similar negative Eu anomalies except JM1/2 which has a strong positive Eu anomaly (2.62). Although the samples JM3/4, JM5/6, JM6/1, and MC3/2 are LREE enriched, but the extent of LREE/HREE fractionation is much more different than others. The REE pattern and abundance of JM5/6 are very much similar to the overlying aeolian sediments. Kaolinite rich samples have very high abundance of REE with similar patterns including negative Eu anomalies. The REE geochemistry of JM6/1 and MC3/2 seem to be attributed to its mineralogical composition. These two samples also have high abundance of Zr and Ti.

## **6.4 DISCUSSION**

The pegmatites of Delhi and Haryana are intrusive into Delhi quartzite and are enveloped by altered and friable quartzite closer to the contact. The pegmatites

**Table 6.5: REE chemistry of alteration products (sand and clays)**

	JM6/1	JM1/2	JM2/3	JM3/4	JM4/5	JM5/6	MC2/1	MC3/2	MC4/3	MC5/4
Ce	115.25	7.43	12.16	21.23	7.28	54.44	40.06	101.47	10.62	11.42
Nd	40.80	3.01	4.70	11.14	4.26	31.95	18.37	48.43	6.46	6.38
Sm	6.61	0.66	0.93	2.06	0.80	6.16	3.03	8.67	1.12	1.14
Eu	1.14	0.54	0.19	0.43	0.15	1.34	0.57	1.67	0.23	0.23
Gd	5.57	0.60	1.03	1.76	0.74	5.61	2.36	6.47	1.01	1.05
Dy	2.30	0.54	1.04	1.18	0.79	5.34	2.92	5.91	1.04	0.92
Yb	2.29	0.39	0.53	0.44	0.39	1.82	1.56	3.23	0.42	0.45
CeN/Yb N	12.90	4.91	5.91	12.37	4.74	7.64	6.58	8.02	6.46	6.47
Eu/Eu*	0.56	2.62	0.60	0.67	0.60	0.69	0.63	0.66	0.65	0.63

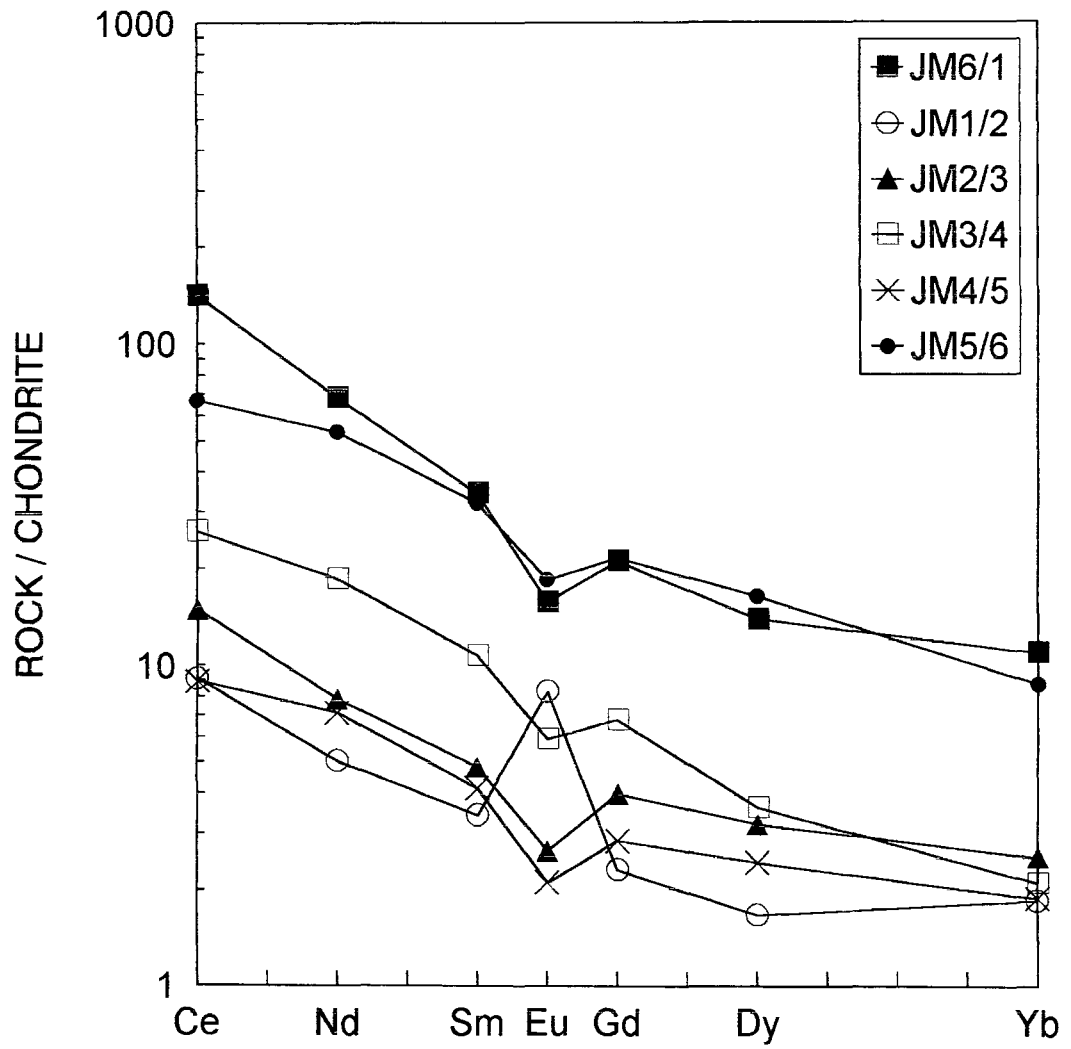


Figure 6.5: REE patterns of clay and sands of alteration zones of Mohabtabad.



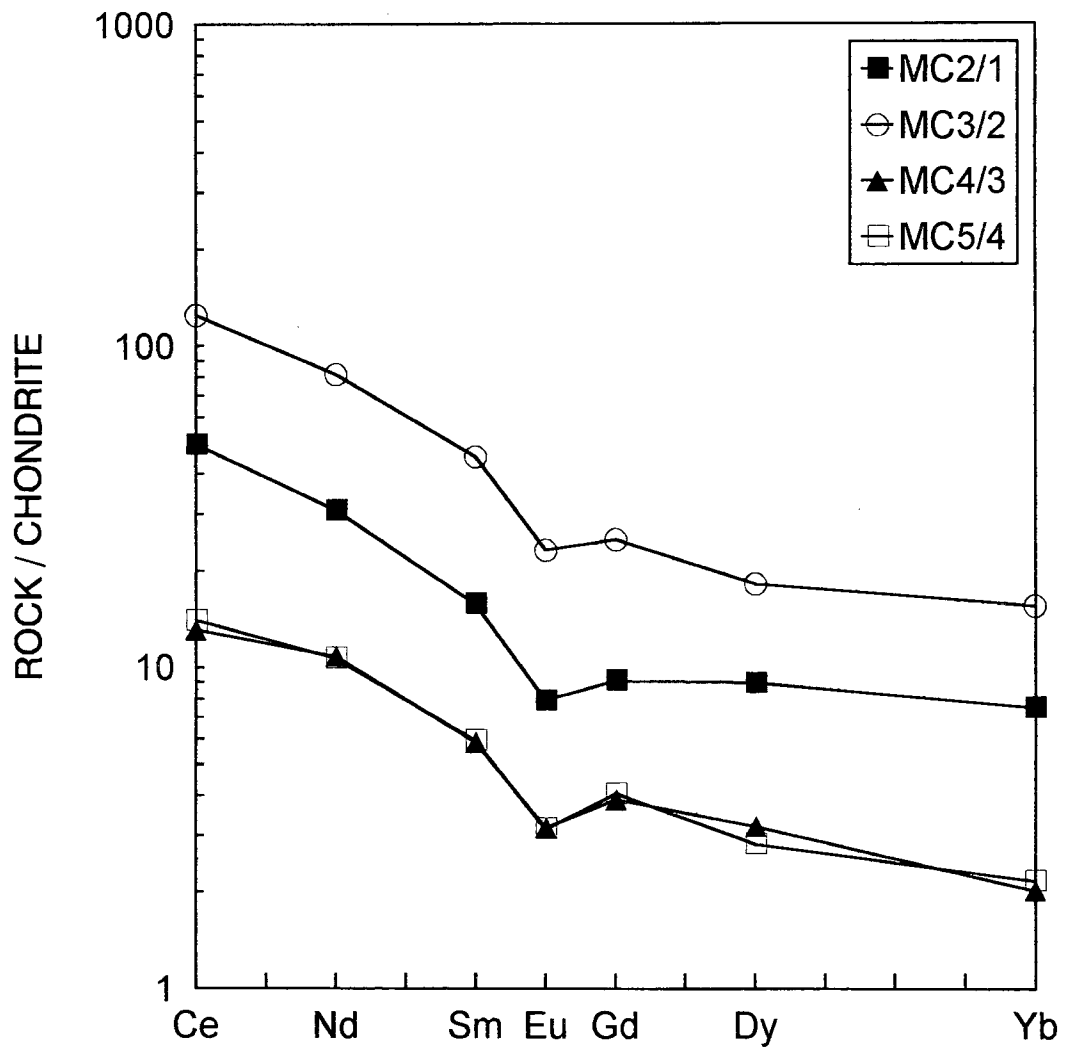


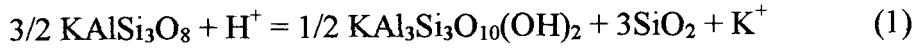
Figure 6.6: REE patterns of clay and sands of alteration zones of Mohabtabad Chouki.

themselves have been altered to kaolin rich pockets with crystals of large subhedral quartz.

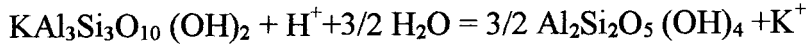
Although minor amount of sericite has been found in some of the samples, kaolinite is by far the most abundant alteration product. Quartz grains are abundant in wall rock zones. Muscovite flakes and tourmaline grains are also seen in clay pockets. The very pervasive nature of alteration in pegmatites had made it difficult to obtain a fresh unweathered sample for the comparison.

The alteration processes such as K-silicate alteration, sericitisation, and tourmalinisation take place at temperatures greater than 300 °C and salinity between 5 and 10 equivalent % NaCl, (Emmermann et al., 1975), whereas most argillic alteration occurs at much lower temperature and salinity (Alderton et al., 1980). Recent stable isotope and fluid inclusion studies favour an origin from deep weathering or low temperature hydrothermal fluids for argillic alteration zones in the porphyry Cu deposits. In the study of Calabona porphyry Cu deposits, Stefanini and Jones (1996) suggested that the continuous inflow of meteoric water downward and the general temperature decrease in the system, produced progressively more oxidised and acidic fluids, which caused phyllic and argillic alterations.

The stability of feldspar, micas and clays is commonly controlled by hydrolysis, in which  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$ , and other cations are transferred from the mineral to solution and  $H^+$  enters the solid phases (Hemley and Jones, 1964; Lasaga, 1995). For instance the stability of K feldspar and muscovite at temperatures below 300 °C is limited by following reactions:



Feldspar                      Muscovite                      Quartz



Muscovite                                      Kaolinite

At higher temperatures, pyrophyllite and andalusite are the stable products instead of kaolinite and quartz (Figure- 6.4).

Calculations and graphic display of the stability in hydrolysis reactions are conveniently handled by many workers using the equilibrium constant, which for reaction -(1) is -

$$K = a^{1/2} \text{ muscovite} \cdot a^3 \text{ quartz} \cdot a \text{ K}^+ / a^{3/2} \text{ K-feldspar} \cdot a \text{ H}^+$$

because all solid phases and water are pure end members,

$$K = a \text{ K}^+ / a \text{ H}^+,$$

which is a function of only the temperature (Rose and Burt, 1979). Using this simplification, Figure-6.4 illustrates the stability of feldspars, micas and aluminium silicates in the familiar plot of K/H versus temperature (Montoya and Hemley, 1975).

The reaction mechanism and activity diagram show that the kaolinite deposits originated after alteration of pegmatite minerals in the direction from K-feldspar-sericite-kaolinite. It has been found by Alderton et al (1980) that during sericitisation of granite Zr, Ti, and P remain relatively immobile, while in the kaolinisation of granite these elements become mobile and apatite breakdown may release phosphorous. This phosphorus may form amorphous phases like florencite (Braun et al., 1993) which are reported to occur in weathered pegmatites (Clark, 1984), and also it can take up to 9

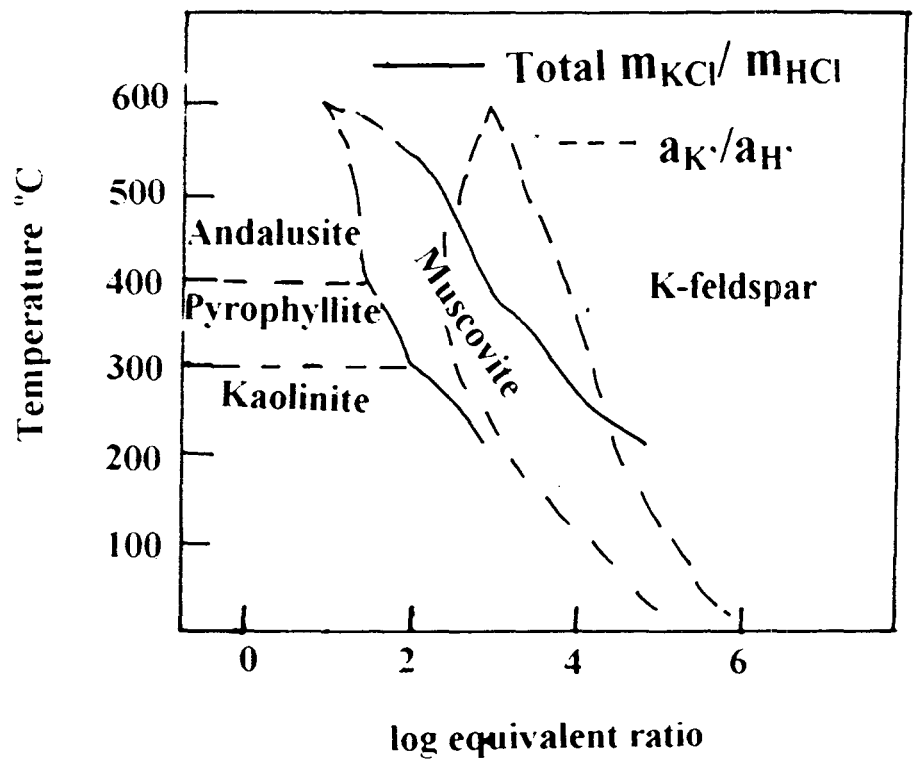


Figure 6.4: Stability of K-feldspar, muscovite and kaolinite in the K/H versus temperature diagram (after Montoya and Hemley, 1975).

weight % of Sr (Mackie, 1962). Alderton et al. (1980) found that in sericitisation there is no REE mobilisation excepting Eu, whereas kaolinisation can cause LRRE depletion during hydrothermal alteration of feldspar. But formation of florencite could be responsible for the high LREE and Sr in JM6/1 and MC3/2 samples.

Braun et al. (1993) have shown that the released elements during weathering can be incorporated in newly formed crystalline or amorphous phases or adsorbed on the clays (Braun et al., 1993). Casey et al. (1993) suggested that weathered layers on silicates have high sorptive capacity. These leached layers may hold the HFS elements effectively. Thus high REE, Ba, Sr, Ti, Zr, Y and Cr in JM6 and MC3 may be due to the absorption to the sericite and kaolinite clay minerals and probably due to the presence of florencite mineral.

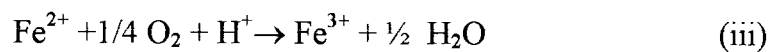
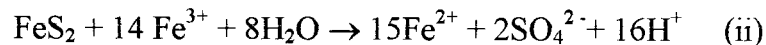
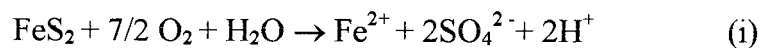
Michard and Albarede (1986) have suggested that unless water/rock ratios in excess of  $10^5$  are achieved at depth during hydrothermal alteration, mobility of REE in granites and shales of continental crust containing high REE, would not be achieved. So, nearly 100 to 140 times Ce enrichment (chondrite normalised) in MC3/4 and JMC6/1 with respect to feldspars of pegmatite origin, which have nearly 0.1 to 1 time Ce (Walker et al. 1986), could be possible only if these were mobilised and concentrated within clay from protoliths and there was no loss of REE during the process. The transport of the materials in wall rock alteration could have occurred either by infiltration (mass movement due to fluid flow through the rock) or by diffusion (transport by diffusion of chemical species through stagnant pore fluids) or by combination of both processes (Rose and Burt, 1979). As it has been shown that the high concentration of immobile elements in these zones can be attributed to the

adsorption to the clays, importance of their apparent increase due to their density change of weathered materials can not be ignored (Brimhall, 1987). The change in density due to the alteration processes and therefore increased porosity must have helped in the mobility of hydrothermal fluids and extensive leaching of mobile elements.

The rare earth elements have very similar chemical properties. They are generally considered to be resistant to fractionation in supracrustal environments (Nance and Taylor, 1977). The resistant behaviour together with their low solubility has been used to identify the parental materials of supracrustally altered rocks and sediments. However, mobilisation and fractionation of the REE can occur during surface alteration of rocks (Nesbitt, 1979; Condie, 1995). REE fractionation in supracrustal environments has been a function of ground water pH and the type of secondary mineral formed (Nesbitt, 1979; Lewis, 1997). In the hydrothermal alterations the mobilisation and fractionation of REE has already been reported (Alderton et al., 1980; Michard and Albarede, 1986; Lewis et al., 1997). Recently it has been also realised that the complexing of REE with ligands and their thermodynamic behaviour are also responsible for the REE fractionation. (Wood, 1990; Gammons et al., 1996)

Wood (1990) has suggested that the trivalent REE and Y should exhibit strong electrostatic complexing with 'hard' ligands such as fluoride, sulphate, phosphate, carbonate, and hydroxide on the basis of experimental data. Extrapolation of available low temperature stability constant data indicates that the stability of all the trivalent REE increase relatively rapidly with temperature, as expected for complexation between hard metal ions and hard ligands (Wood, 1990). It has been suggested that sulphate complexes are most important at acidic pH and that the carbonate

complexes become predominant at basic pH. Wherever abundant sulphides may accompany REE mineralisation, oxidation of sulphides during weathering may provide sufficient sulphate to transport the metals. The pyrites in the quartzite and their dissolution in surfacial weathering must have provided sulphate. The hydrothermal solution percolating through the quartzite and pegmatite has oxidised the pyrite to generate the sulphate anion. Although, the solubility of pyrite are quite low, but they are unstable in aqueous environments where they are exposed to oxidants such as dissolved oxygen or ferric iron (Singer and Stumm, 1970; Moses et al., 1987). Reactions (i) and (ii) illustrates the breakdown of pyrite with dissolved oxygen and ferric iron. Reaction (iii) represent the regeneration of ferric iron.



The oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  is responsible for the fixation of  $\text{Fe}^{3+}$  in the form of goethite in the weathering rinds and morrum sands. Powell (1974) noted on the basis of stability constants of REEs as a function of atomic number that, the sulphate complexes show very little preference between the LREE and HREE. Therefore little or no fractionation of the REE is expected due to aqueous sulphate complexing alone. The absence of REE fractionation in the samples (JM1/2, JM2/3, JM4/5 and MC2/1, MC3/2, MC4/3, MC5/4) must be due to predominance of sulphate anions in the weathering solution. The REE fractionation in JM3/4, JM5/6, JM6/1 and MC3/2 may be due to some other reason. For the JM6/1 and MC3/2 the mineralogical composition may have controlled their REE patterns and abundance. JM5/6 could have inherited its

pattern from the overlying sediments and that is why its abundance is also higher due to incorporation of overlying materials by downward transport of finer grains (Brimhall et al., 1991). Compared to others, the HREE depleted pattern of JM3/4 can be explained by the supply of carbonate complexes from the overlying sediments for the preferential complexing with HREE. The stability constants of carbonate complexes increase with atomic number, so it favours the HREE mobilisation (Wood, 1990). Nesbitt (1979) has also suggested the greater mobilisation of HREE in weathering of Torango granodiorite resulting from preferential formation of complexes with carbonate ligands.

The red sand of JM5/6 underlies a thick aeolian silt deposit and shows enriched REE pattern very similar to overlying sediments. Whereas, similar sand (MC5/4) which lacks any sediment/soil profile overlying this, shows its REE pattern and abundance similar to adjacent sand. This REE enrichment in JM5/6 is also corroborated with enrichment in other major and trace elements. The enrichment must be due to the illuviation of silt and clay size particles in suspension. LREE/HREE of JM5 is very similar to the overlying aeolian silty deposit (see Chapter-7). It should be noted that, despite of the similarity in major and trace element chemistry of JM5/6 and JM2/3, the later does not show similar REE enrichment. This also substantiate a mixing of overlying sediment to the JM5/6.

Fluoride complexes also show a steady increase in stability with increasing atomic number (decreasing ionic radius) but in the neutral to basic condition only carbonate is important for the REE transport (Wood, 1990). In the overlying sediments the abundance of calcrete nodules suggest predominantly a basic condition in upper horizons. While, in the deeper levels, acidic condition must have prevailed due to pyrite

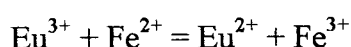


dissolution. The other sampling site (Mohabtabad Chouki) seems not to have affected by carbonate as there was no supply, because that site is basically devoid of transported alkaline sediments. Thus, sulphate complexes were important for REE transport in the zones where carbonates couldn't reach due to its exhaustion under the predominance of acidic environment.

It has been found that the sample JM1/2 has a prominent positive Eu anomaly, but highly depleted in other elements. Although Eu and Sr should behave similarly (Philpotts, 1970; Drake, 1975) this may not be correct for water-rock interaction (Michard and Albarede, 1986). The high Sr in JM6/1 and MC3/2 could be attributed to the concentration of florencite, an alteration product of apatite found in weathered pegmatites, which can take up Sr as much as 9 weight % (Henderson, 1984). The florencite are highly enriched in LREE with negative Eu anomaly (Braun et al., 1993). Thus, high REE and Sr in these two zones possibly could have been provided by the florencite formation. It is also possible that the Eu and silica could have been mobilised during the breakdown of feldspar to sericite in the JM6/1 zone (Alderton et al., 1980). The hydrothermal solution enriched in silica and Eu must have had positive Eu anomaly as found in other hydrothermal fluids (Michard and Albarede, 1986; Michard, 1989; Lewis et al., 1997). The coarser quartz grain size of JM1/2 with respect to adjacent JM2/3 (medium to fine grained quartz) also indicates that there has been an overgrowth of quartz grains at later stages through the precipitation of silica on the smaller grains (Dove, 1995). It has been also reported that the hydrothermal solution imparts +ve Eu anomaly to the sinters deposited by them (Lewis et al., 1997). So, compared with pure quartzites of this area (JM9), JM1/2 has lower REE abundance

with strong positive Eu anomaly, suggesting its precipitation from the fluids containing similar REE characteristics.

Michard and Albarede (1986) suggested that the much higher values of Eu/Eu\* in the hydrothermal solutions may be due to the divalent state of Eu in fluids as a result of strong displacement of the right hand side of the equilibrium:



in the solutions that contain ferrous iron as an abundant cation. Apart from the chemical change of II oxidation state to III oxidation state of Eu, the ferrous ion also played a major role in the dissolution of quartz. So, during the feldspar weathering Eu<sup>2+</sup> could have been released to the solution and reprecipitated, as it oxidised to Eu<sup>3+</sup>, in the zone of JM1/2.

Morris and Fletcher (1987) suggested that the reaction of iron with quartz on the grain surfaces is responsible for silica removal. Ferrous iron are generated when dissolved oxygen or Fe<sup>3+</sup> react with pyrite in aqueous environment (Singer and Stumm, 1970; Moses et al., 1987). The reaction of ferrous ion of circulating water formed a hydrous ferrous ion/silica surface layer. These layers broke down in oxidising conditions to a goethite precursor and the silica was released to solution (see Chapter-5). This mechanism could be important for weathering of quartzite to form red friable sands (e.g. JM3/4, JM5/6, MC5/4) surrounding the altered pegmatites.

**Present day geothermal condition and its implication to alteration processes:** It has been found that the hydrothermal alteration is often accompanied by hydrothermal ore deposits and active geothermal systems (Inoue, 1995). Recently Raval (1995) has reported that anomalous heat flow at Tosham (around 100 km away of Delhi) and hot

springs at Sohna area (Gurgaon district of Harayana) on Delhi ridge. Raval (1994) has explained that the plausible channels in the Delhi -Haradwar ridge may episodically carry the fluid and heat away from the Himalayan topographic front. He explained that, the subduction /collision boundary could, at least transiently, get loaded with fluids and heat. The sudden uplift may also give rise to high thermal gradient (in excess of around 80 °C/km). The northward extension of basement heterogeneity forms a sort of T-junction with the Himalayan collision front and hence they provide the deep permeable channels (or conduits) along which relatively large scale flow of hot fluids from the orogenic front could be focused into the subcontinent. Expulsion of hot fluids from the Himalayan topographic front into the subcontinent would cause significant electrical conductivity anomalies (Figure-6.7). This is strongly supported by the presence of high (electrically) conducting layer as inferred by Lilley et al. (1981). The trend of this deep conductor nearly coincides with the Delhi Haradwar basement heterogeneity (Figure-6.7). The trends of basement heterogeneity are also expected to overlap with high heat flow trends due to the (a) channelling of hot fluids, and (b) high thermal conductivity of the basement ridges owing to their higher grade of metamorphism (Wenk and Wenk, 1969). It has been found that the high temperature and heat flow coincide with higher basement topography (Demming et al., 1992). This corroborated from spatial distributions of both the surface heat flow and the hot springs (Figure.7). The anomalous high heat flow values at Tosham (around 95 mw/ m<sup>2</sup>) and Khetri (around 70 mw/m<sup>2</sup> ) recorded by Gupta et al. (1989) and thermal spring at Sohna could be due to the hot fluids from the collision boundary reaching deep within the regions and later slow conductive heat transfer coming into play.

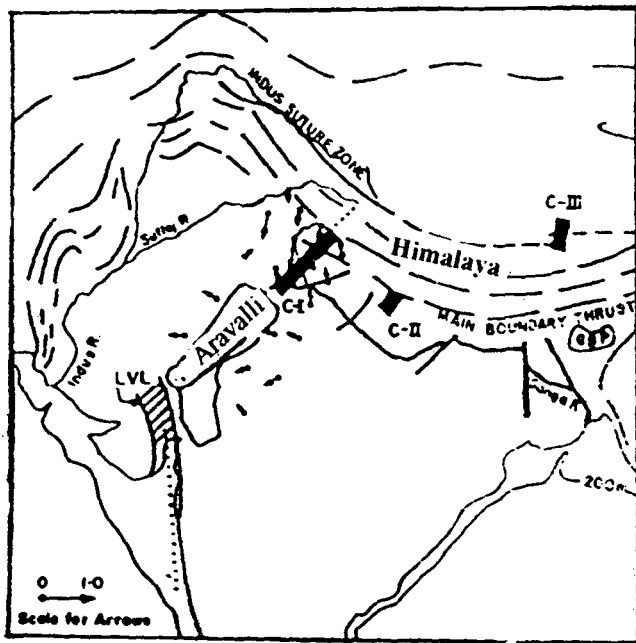
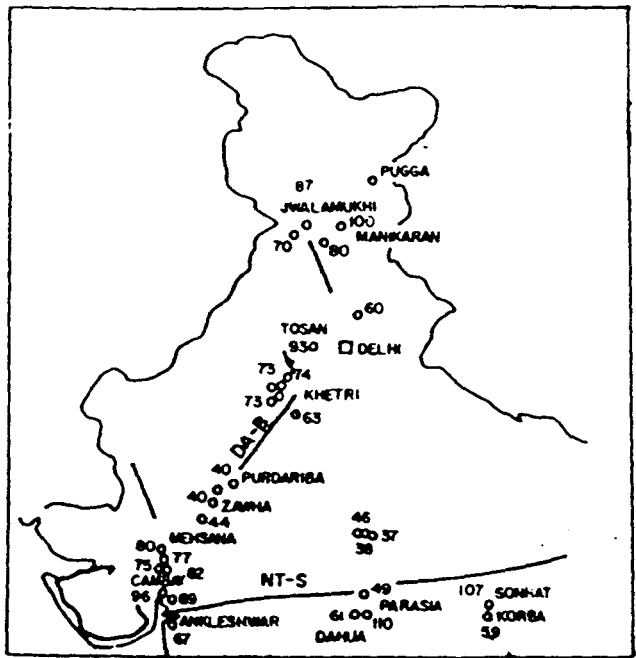


Figure 6.7: (A) Heat flow over northern India, (B) Electrical conductivity over Indian sub-continent, (after Raval, 1995).

The descending meteoric water under such conditions get heated up in deeper levels due to higher geothermal gradient and therefore could have facilitated alteration of wall rocks. Many of the geothermal systems are reported to have given rise to argillic alteration due to their hot water and low pH condition (White et al., 1971; Schoen et al. 1974; Meyer and Heamley, 1967). Rose and Burt (1979) have explained that the alteration at hot springs and geothermal systems have at least two distinct environments and types of alteration. Beneath the water table the hydrothermal fluid is near neutral or weakly alkaline with chloride as major ion. The alteration products in felsic rocks are feldspars micas, zeolites, silica minerals, montmorillonite and occasionally kaolinite. In contrast to other hot springs and geothermal systems, near surface fluids are acid, have high  $\text{SO}_4^{2-}$  and Cl, Fe, Mg, Ca, aluminium and relatively low sodium and potassium (Raymahashay, 1968; White et al., 1971). Here the alteration is of advanced argillic type containing kaolinite, alunite and other sulphates, sulphur, silica minerals and zunyite. It can be suggested that the high geothermal condition on the Delhi ridge could have facilitated the extensive hydrothermal alteration of pegmatites and quartzites to kaolinite and silica sand deposits respectively.

## **6.5 CONCLUSIONS**

The hydrothermal alteration of the pegmatites and quartzites to kaolinite and silica sand respectively have been mainly attributed to the nature of rock types, nature of the hydrothermal solution, and prevailing geothermal condition. On the basis of this study it can be concluded that: (a) the first step towards the clay and sand formation were the

intrusion of pegmatites, (b) the second step were hydrothermal alteration processes under the present geothermal condition, (c) the feldspar of pegmatites first weathered to sericite and then intensive leaching caused formation of kaolinite, (d) for the origin of silica sand and ferruginous sand different mechanism seem to have been responsible, i.e., for the silica sand formation primarily pegmatitic impact and secondarily alteration of feldspar was responsible and, for the ferruginous sand particularly ferrous-ferric complexation and silica removal was responsible, (e) transportation and mixing of overlying sediments with weathered quartzite affected the geochemistry of the uppermost horizon of sand deposit, (f) the heated meteoric water, which had acidic nature because of pyrite dissolution, was responsible for the alteration, but basic weathering condition also prevailed just below the transported sediments/soil to a few meters depth, (g) under the dominance of sulphate complexes REE were quantitatively mobilised, but locally particularly near the surface carbonate complexes were also important in the REE fractionation, (h) high REE and Sr in JM6 and MC3 could be attributed to the florencite mineral, which were formed after apatite weathering/alteration, (I) the hydrothermal solution with low REE abundance and strong positive Eu anomaly imparted its character during silica precipitation on to the growing quartz grains of JM1/2, and the Eu has been provided during sericitisation in JM6 zone.