3. Materials and Methods

3.1 Sample details

Representative samples of different morphological varieties of manganese and iron ores and associated litho types were collected from the study area in a most systematic way from the location shown in Fig. 4.2. Representative fractions of the sample were ground to below 200-mesh size by conventional grinding methods for further geochemical studies. Polished sections of selected numbers of manganese and iron ore varieties were prepared for microscopic and microprobe studies, for detailed mineralogical and compositional analysis.

3.2 Mineralogical Studies

Mineralogy of ore types and the associated rocks from the study area has been established by synthesizing the integrated results brought out through the following instrumental methods.

3.2.1 Optical microscopy

The various types of litho types and ore specimens are cut to small sizes by a diamond wheel saw (Carl Zeiss) and Isocut slow speed saw (Buehler make) and different samples are prepared to study under reflected and transmitted light microscopes.

For ore microscopic study, the samples were polished by conventional polishing techniques, cleaned ultrasonically and examined under Orthoplan Microscope (Leitz make). The mineralogy, texture, microstructure, grain size distribution pattern and inclusions etc. in respect of various ore types were established by this study.

For petrography study, thin sections of selected samples were prepared by usual techniques and examined under Ortholux microscope (Leitz make). This study helped to know the nature, distribution and textural pattern of associated litho types.
3.2.2 Electron microscopy

Unlike optical microscopy where light is the source for image formation, in electron microscopy, the image formation is due to the scattering of electrons as the electron beam scans over the sample. In general, this study covers two major aspects: 1) it brings out the size, shape and morphology of minerals and their textural pattern by using a scanning electron microscope (SEM) and 2) it gives thorough knowledge about exsolution, intergrowth, inclusions, solid solutions and composition of different phases by using a Wave Length Dispersive Spectrometer (WDS).

For SEM study, natural sample (5 x 5 x 5 mm size) was first coated with ultra thin film of gold by an ion sputter JFC-1100 and then was exposed under a Japanese make electron microscope (JEOL, JSM-35CF). For this purpose, the working height was kept 15 mm with working voltage ranging between 10 kV to 25 kV.

For WDS, polished samples were taken and examined at 39 mm working height. The working voltages for study were kept at 25 kV with beam current 100 nA. By this technique, X-ray image mapping was directly photographed from the oscilloscope with the help of a camera.

3.2.3 X-ray diffraction

X-ray diffraction technique (XRD) was extensively used for identification of various mineral phases and assessing the abundance of each phase in a sample. The XRD was carried out by means of Phillips Diffractometer (PW-1710) having automatic divergence slit, receiving slit and graphite monochromator assembly. Cu Kα radiation operating at 40 kV and 20 nA was used for this purpose. A diffraction pattern recording the angle 2θ against the intensity was obtained over a range between 10° to 70° corresponding to d-values between 9 Å and 1.68 Å. The scanning rate was 2° per minute with recorder full scale set into 2 x 10^3 counts. Each mineral phase exhibits a characteristic reflection peak of its d-values. This set of d-values was matched with JCPDS data book (1980) and various minerals were identified. Further, the variations in
the peak intensities of different mineral phases in the ore sample indicate their relative abundance

3.3 Chemical Studies

Composition of different mineral phases in the solid state was determined using electron probe micro-analysis (EPMA) technique. The major, minor, trace and REE constituents in different types of ores and associated lithotypes were taken up by classical method and using different instrumental techniques such as XRF and ICP-MS.

3.3.1 Electron microprobe

The chemistry of different phases in selected samples was determined by means of Electron Microprobe. The Jeol make 8600 Superprobe (take-off angle of 52.5 degrees) in the Institute of Instrumentation Centre, IIT, Roorkee, which is equipped with three spectrometers and four different crystals (LiF, PET, ADP, TAP), operated at 15kV accelerating voltage and 15 nA sample current was used for this purpose. The matrix corrections of the intensity measurements were made using the ZAF correction programme by Bence and Albee (1968).

Electron probe microanalyses of some samples were also taken up at RRL, Bhubaneswar, India using a Jeol super probe (JXA-8100). For this study, polished samples were prepared and quoted with carbon by a vacuum coater. The working voltage was kept 20 kV with beam current as 40-100 nA. Area scanning mode was used for qualitative analysis and X-ray scanning to find out elemental distribution. Quantitative analysis was taken up with the help of pre-set automatic programmable point scanner using silicate standards and on-line ZAF correction procedure.

3.3.2 X-ray fluorescence

Major and minor constituents of various ore/litho-units were analysed by XRF Spectrometry on Phillips (PW-1400) X-ray spectrometer with Scandium and Rhodium targets using Pentaerythritol (Al, Si), Thallium Acid Pathalate (Na,
Mg), Germanium (P) and Lithium Fluoride (LIF, for heavier elements) as analysing crystals in vacuum medium.

International and in-house standards of appropriate compositions were used for calibration. Both major and minor elements were determined in pressed powdered pellet technique.

### 3.3.3 Inductively coupled plasma-mass spectrometer

The trace and rare earth elements (REE) in both ore and associated litho units were analysed at NGRI, Hyderabad, India, using Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). The ICP-MS used was a Plasma Quad PQ1 (Fisons Instruments, UK) controlled by an IBM PC-XT micro-computer and associated software. The ion-detection system and the data acquisition system consist of a Channeltron Electrom Multiplier (CEM) and a multichannel analyser (Tracor Northern).

To analyse the trace and REE, the standard acid dissolution procedure was adopted for sample preparation as prescribed by Balaram et al., 1989. Sample solutions were prepared by HF-HNO₃ acid digestion with Indium (100 mg/ml) as internal standard. To ensure precision of the data, a set of international ore standards of different chemical compositions (NNODA-1, MNODP-1 etc.) was analysed along with the samples.

### 3.4 Beneficiation Studies

Different types of low/off grade manganese ores such as iron-rich, silica-rich, and alumina-rich from selective mines were subjected to beneficiation studies to evaluate the prospects of their optimum utilization. Various types of samples were crushed to below 2mm size by roll crusher at different settings and classified into different fractions using standard sieves (2mm, 1mm, 0.5mm, 0.3mm, 0.15mm, 0.075mm). Beneficiation studies were undertaken using magnetic separation, gravity separation and desliming techniques. The individual beneficiation methods are described below.
3.4.1 Heavy Media Separation

Sink and float studies were carried out using bromoform having 2.85 specific gravity. The aim of these studies is to assess the liberation characteristics of silica and other gangue minerals from the manganese ore. The ore sample was ground to -100 mm by stage crushing by roll crusher at different settings. The crushed sample was size analysed by using standard test sieves. The closed size fractions so obtained were used in these studies. About 500 gram of the closed size fraction was taken and separated using bromoform. The heavies and lights were collected separately, washed, dried, weighed and analysed for Fe, Mn and SiO₂. These studies were carried out on the following samples: (1) -1 00+0 5mm, (2) -0 5+0 3mm, (3) -0 3+0 15mm and (4) -0 15+0 075mm. The extent of liberation was assessed in each case.

3.4.2 Mineral Separator

In view of density difference between manganese and silica/alumina, preliminary beneficiation studies of low-grade siliceous Mn-ore sample were carried out using Mozley Mineral Separator to assess the amenability of beneficiation by gravity methods. About 500 gm of closed size fractions viz. -1 00+0 500mm, -0 5+0 3mm, -0 3+0 15mm, -0 15+0 075mm and -0 075mm were taken separately and subjected to mineral separator for 15 minutes at 20 lit/min wash water rate. Then both heavies and lights were collected separately, dried, weighed and analysed. The recovery of manganese in each case was calculated separately. Then over all recovery was computed from these results.

3.4.3 Dry Magnetic Separation

Laboratory scale beneficiation studies of all the sample types were carried out by using a dry belt magnetic separator supplied by M/s Box-Mag Rapid Limited, England. Initially, studies were carried out to optimise the process parameters. The effect of particle size, magnetic intensity was evaluated. The closed size fractions of manganese ore were prepared by roll crushing and dry sieving. Each fraction was subjected to magnetic separation at different magnetic intensities. About 1.0kg of sample was taken and subjected to separation at...
different magnetic intensity. First magnetic intensity was optimised for each fraction. The same intensity was used for all other fractions. Both magnetic and non-magnetic fractions were collected, weighed, and analysed for Mn, Fe, SiO$_2$ and Al$_2$O$_3$ content (in specific samples). The same procedure was followed for all the experiments. All the studies were carried out on coarse size fraction up to +0.075 mm size. The -0.075 mm fraction is subjected to wet magnetic separation.

### 3.4.4 Wet Magnetic Separation

Selective samples were studied using wet high intensity magnetic separator (WHIMS) supplied by M/s Box Mag Rapid, England. The magnetic intensity of the instrument was varied by grid gaps and applied current. Prior to magnetic separation, the sample was first conditioned for 10 minutes. After proper conditioning, the slurry was then passed through the magnetic separator. The magnetic fraction was retained in the grid where as the non-magnetic fraction was collected at the bottom. Both the magnetic and non-magnetic fractions were dried and analysed to check the purity and recovery of the product.

### 3.4.5 Gravity Separation

Beneficiation studies of some low-grade Mn-samples were carried out using 1016-x 457 mm Denver Wilfley Laboratory Table supplied by M/s DENVER, USA. The sample was reduced in roll crusher to -2.0 mm by stage crushing. The 2.0 mm sample was ground in a ball to prepare -0.5 mm sample by closed circuit grinding method. Then the ground sample was subjected to classification to produce different size fractions viz, -500+150 micron and -150 microns. These size fractions were used for tabling studies. About 10 kg of sample was mixed with 20 liters of water and made uniform slurry. This slurry was pumped to table feed box at uniform rate of 20 kg/hour. The wash water was maintained at 6 liters per minute and stroke length was kept at 10 mm. The -500+150 micron fraction was processed on coarse table and -150-micron
fraction was processed on slime table. Different products obtained in each case were collected, dried, weighed and analysed.

### 3.4.6 Desliming and Tabling

Lot of fines is generated during grinding of the sample to −500 micron due to friable nature of the ore. These slimes are interfering in gravity separation process by Tabling. The −150 micron fraction was deslimed in hydro cyclone. These desliming studies were carried out using Mozley Hydro cyclone Test kit supplied by M/s Mozley, England. 60mm hydro cyclone with 14.3mm vortex and 6.5mm apex was used in these studies. About 5.0kg sample was mixed with 20 liters of water and uniform slurry was prepared. Then the slurry was pumped to hydro cyclone at uniform rate at 15-PSI pressure. The underflow and overflow were collected simultaneously. The experiment was repeated to treat 20.0kg of sample under identical conditions. The underflow and overflow were weighed and analysed. The underflow sample was subjected to Tabling under similar conditions used earlier. Both the results of desliming and without desliming were compared.