MINERALOGY, PETROLOGY AND GEOCHEMISTRY OF MANGANESE MINERALIZATION AND ASSOCIATED ROCKS IN SAIDGI AND SHUIDAR AREAS, NORTH WAZIRISTAN

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UNIVERSITY OF PESHAWAR.

DEDICATION

DEDICATED TO AL MIGHTY ALLAH

MINERALOGY, PETROLOGY AND GEOCHEMISTRY OF MANGANESE MINERALIZATION AND ASSOCIATED ROCKS IN SAIDGI AND SHUIDAR AREAS, NORTH WAZIRISTAN

THESIS

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ABSTRACT

North Waziristan is dominantly composed of rocks of the Waziristan ophiolitic complex, Indian plate and the quaternary deposits. The ophiolite complex is composed of ultramafics, gabbros, sheeted dikes, pillow lavas, pelagic sediments and plagiogranites which are overlain by massive sedimentary sequences. The rocks of the Indian plate are mainly limestone, shale and sandstone of Jurassic to Cretaceous age. The quaternary deposits occur as heterogeneous material of variable size.

The Saidgi and Shuidar Mn-deposits are a part of the Waziristan Ophiolitic complex. These deposits are banded and massive in nature and hosted by metachert. In Shuidar area the Mn-ore bodies are generally banded by having Mn-rich layers alternating with the metachert. The Saidgi ore bodies are generally massive in character and are in the form of lenses. The metacherts are finely crystalline, thin to medium bedded hard rocks. These are generally overlying the metavolcanics (pillow basalts) in the study area. Both Saidgi and Shuidar ore bodies are having braunite as the Mn-bearing mineral. Braunite and cryptocrystalline quartz are the main constituents, however, the Shuidar ore bodies have hematite as an additional phase. The chemistry of braunite has similarity with the natural braunite and also with that of the Mn-deposits found in ophiolites- else where in the world. The metacherts of both Saidgi and Shuidar areas have similar field and mineralogical characteristics. These are exceedingly microcrystalline aggregates of microcrystalline quartz, chalcedony, and lesser hematite.

Chemically the Saidgi Mn-deposits have higher MnO, and lesser SiO_2 *and* Fe_2O_3 *as compared to that of Shuidar Mn-deposits. The Shuidar Mn-deposits, however, have higher amount of trace elements (Cu, Pb, Zn, Ni, Cr, Co) relative to that of Saidgi Mn-deposits. Both these deposits are characterized by low Fe/Mn ratio. Majority of the major and trace element data fall within the fields defined for hydrothermal Mn-deposits in various discrimination diagrams and, therefore, have no relation with hydrogenous deposits. Metacherts of Saidgi and Shuidar areas are similar in chemical composition. These have Fe/Mn ratio typical of hydrothermal origin.*

Both Saidgi and Shuidar Mn-deposits are spatially separated from each other but are cogenetic. These were formed by the submarine hydrothermal solution in an ocean floor spreading environment within the Neo-Tethys ocean. These deposits are, therefore, originated along sea floor spreading centers (Mid-ocean ridges) and are later on obducted on land along with the other ophiolitic rocks of the area. This study also suggest that the Saidgi Mn-deposits (~34000 metric tons) are of of greater economic importance as compare to the Shuidar Mn-deposits.

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CHAPTER 1

INTRODUCTION

In Pakistan manganese deposits are mainly situated in Lasbela (Baluchistan) , Chura gally in Mansehra and Federally Administered Tribal Areas (FATA). In FATA manganese deposits are present in North Waziristan, Kurram and Bajaur Agencies, and also some minor showings occur in Mohmand Agency. Among these deposits, manganese of north Waziristan and Bajaur area carries significant economic importance because of its grade and good ifrastructure.

In north Waziristan, Mn-deposits are reported in Saidgi and Shuidar areas (Fig. 1) which have been investigated in detail during this study. Geologically the north Waziristan Agency offers favorable environment , depositional criteria for locating promising manganese deposition. The manganese bearing formation extends from Thal in the north-east to Shuidar in the south-east along Saidgi -Kharsin Datta Khel Barzai line. So far manganese prospects have been identified at Tor Kadi Khel, Tut Narai, Kharsin and four localities around Barzai in Shuidar.

In Saidgi area, near village Tor Kade Khel, the manganese deposit occurs as lensoid body, having micro-bands of interbeded metachert. This area is covered by Survey of Pakistan Toposheet No. 38G/16. It lies at a distance of 5 kilometers (unmetalled road) from the Faqiran Killi, which in turn is connected to the Miranshah (an agency head quarter) by a 21 Kms partly metalled road.

In Shuidar area veins , pockets , lenses and bands of manganese are located at four places on either side of Barzai Khwar. The occurrences are

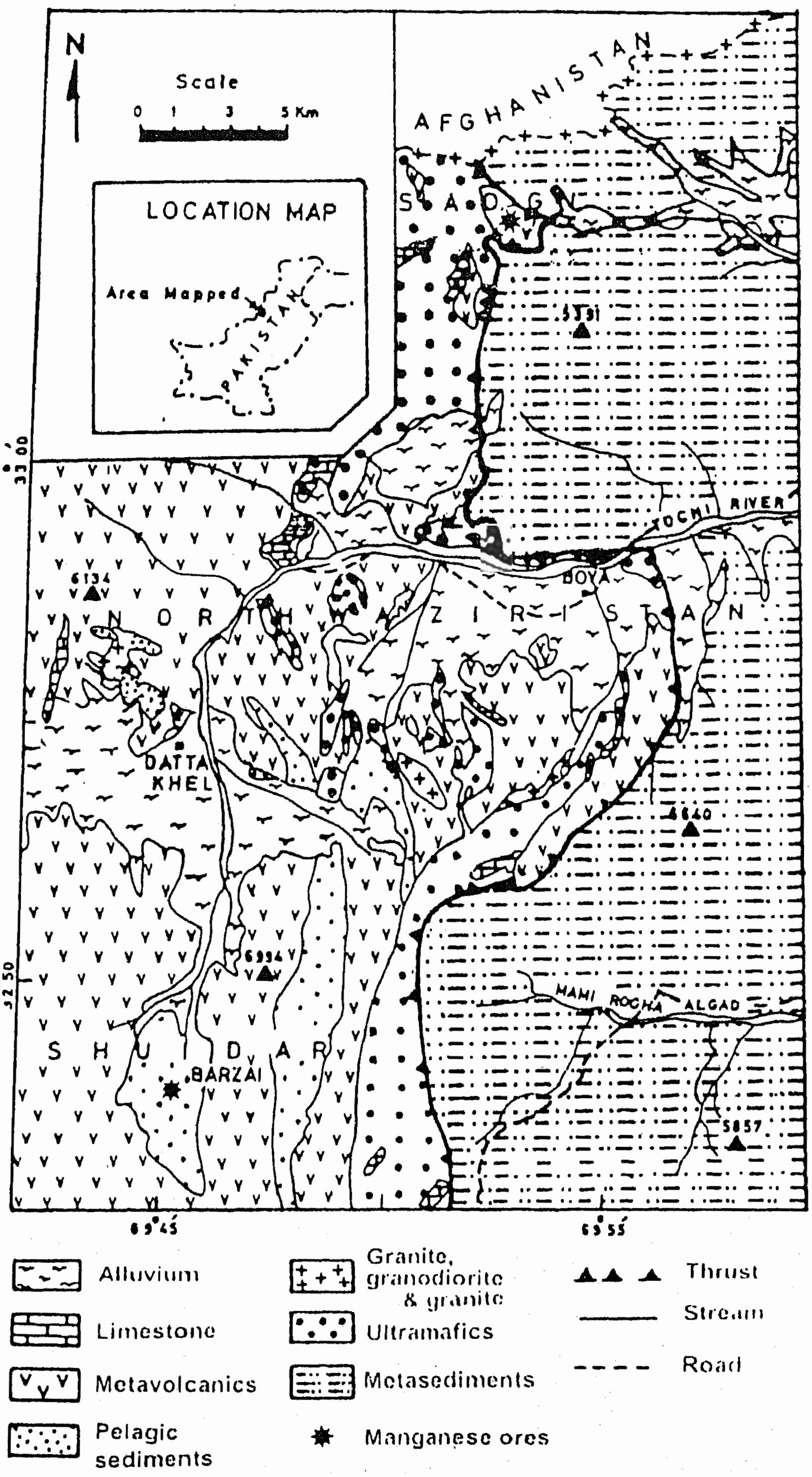


Fig. 1. Geological map of part of the north Waziristan, N.W.F.P., Pakistan (simplified after Badshah, 1985)

roughly located at grid points 385.808,386.798,386.795,366.805 of survey of Pakistan Toposheet No. 38-K/13 at altitude 7000 feet above sea level. Barzai is connected to the main road at Datta Khel by about 13 kilometers fair weather road . Datta Khel lies at a distance of 48 kilometers to the west of Miranshah.

Objective of this study

Both mineralogical and geochemical studies on these deposits (both of Saidgi and Shuidar) and associated metacherts have been carried out during this study in order to accomplish the following aims and objectives:

- To prepare the geological maps of the manganese deposits and adjoining rocks in both Saidgi and Shuidar areas.
- To determine the mineralogical and textural features of these deposits and associated rocks.
- To identify the geochemical characteristics, especially Mn contents, of these deposits and associated rocks.
- To evaluate the economic importance of these Mn-deposits and, if possible, to identify the procedures for the preconcentration of Mn in the raw material.
- To ascertain the possible origin of the Mn-deposits and associated metacherts.

Methodology

Rock samples collected during field were treated for preparing thin sections (both polished and un-polished) for silicate and ore mineralogy. The silicate mineralogy has been carried out by Nickon plane polarized microscope while the ore mineralogy has been carried out by the Nickon metallurgical microscope. The qualitative ore mineralogy has also been carried out by the Rigco X-ray Differactometer powder pattern and the minerals have been identified by the d-spacing values. The chemical analyses of braunite phase have been determined by using the Jeol Electron Microprobe.

Representative samples were then selected for further experimental work. The rock samples were crushed in Jaw crusher and then the crushed chips were pulverized in a tungsten carbide ball mill to 200 mesh size. A portion of individual sample was collected after proper quartering and coning. During this whole process greater care was practiced to avoid contamination. The powdered samples were stored in the air tight glass bottles. These bottles, after removing the lids, were kept in the oven at 110 °C for two hours in order to remove the moisture. The moisture free powders of the manganese ores, metacherts as well as the world known rock standards were dissolved in to stock solutions of known volume by different methods. These stock solutions were used for the determination of major, minor and trace elements by classical and instrumental methods. These techniques involves sophisticated instruments such as atomic absorption and UV/Visible spectrophotometer.

CHAPTER-2

REGIONAL GEOLOGY

The study area is located in the north-western part of Waziristan ophiolitic complex. It covers over 500 km^2 area of the Boya-Razmak region and extends further west in to Afghanistan. This ophiolitic complex occurs as north westerly dismembered ophiolite belt at the western margin of the Indian plate (Bakar and Jackson 1964, Kazmi & Rana 1982). Preliminary mapping of the Waziristan ophiolite was conducted by Khan et al. (1982). A relatively detailed geological map (Fig.1) was published by Badshah (1983; 1985). Jan et al. (1983) and Ahmed and Hamidullah (1985) published a preliminary mineral chemistry of the Waziristan ophiolite complex.

The sedimentary rocks associated with the Waziristan ophiolite are ranging from Mesozoic to early Tertiary in age and are locally covered by Quaternary deposits. The ophiolite occurs as a major thrust sheet over-riding the Jurassic-Cretaceous calcareous sediments of the Indian plate. Eocene sediments mostly limestones and shales, with a red oxidized zone towards their base, unconformably overlie the ophiolitic rocks. This suggest that the ophiolite was tectonically emplaced during Late Cretaceous or Paleocene times . This age is similar to that of the emplacement of Zhob (Ahmad & Abbas, 1979; Allemann, 1979) and Bela ophiolites (De Jong & Subhani, 1979).

The Waziristan ophiolite displays a complex internal structure. The rocks are generally intensely folded, faulted and in places fractured, brecciated and granulated. Typical members of the ophiolites (ultramafics, gabbros, sheeted dikes, pillow lavas, pelagic sediments and plagiogranites) overlain by massive sedimentary sequences are present but do not occur in normal order. This is due to the intense deformation which has dismembered the ophiolitic normal order resulting in a chaotically arranged stack of thrust slices. These ophiolite bodies can be regarded as alochthonous fragments of the Neo-Tethys oceanic crust and upper mantle, formed in the Neo-Tethys basin that probably closed in the Cretaceous and Early Tertiary time (Beck et al., 1992). This ophiolite belt is interesting from economic point of view because of the occurrence of copper, manganese and chromite deposits in the region (Badshah, 1983, 1985; Jan et al., 1985). Copper and Manganese deposits are investigated in detail by Federally Administered Tribal Areas (FATA) Development Corporation. Khan et al., 1982 established a sequence of lithology in the Boya-Razmak area of north Waziristan which is described below:

Age		Lithology.
Quaternary		Channel, piedmont and stream deposits.
	----------- Un-conformity -----------	
Eocene		Limestone and Shale.
	----------- Un-conformity.-----------	
Paleocene (Emplacement age)	(Ophiolite Complex)	Pelagic sediments, volcanic flows and breccia, sheeted dikes swarms, mafic & ultramafic rocks
	-----------Thrust-----------	
Cretaceous to Jurassic.		Limestone, Shale and Sandstone.

ROCKS OF INDIAN PLATE

Jurassic to Cretaceous (un-differentiated) sediments:

These sediments include limestone, shale and sandstone that have north-eastern strike and westerly dip. The limestone is fine grained and gray in clour. It is oolitic, medium to thick bedded and sparsely fossiliferous at places. The shales are gray to black, thin to medium bedded and calcareous with bands of ferrogenous claystones varying in thickness from 2 to 9 meters. The sandstone, forming a persistent unit, is medium-to thick-bedded and fine-to coarse-grained with a black colour due to desert varnish. The assignment of a Jurassic to Cretaceous age to these rocks is based on lithological similarities with the known rocks of this age elsewhere in the region (Khan et al., 1982). A continental shelf environment at the north western passive continental margin of the Indian plate is envisaged for these sediments (Beck et al., 1996).

ROCKS OF THE OPHIOLLITE COMPLEX

The name Waziristan ophiolite complex for the rocks of the Waziristan area has been assigned by Asrarullah et al., 1979; Khan et al., 1982; Shah, 1984; Badshah, 1983; 1985; Jan et al. 1983; 1985. This complex has been traced over a linear distance of more than 30 kms and a width of up to 25 kms in north Waziristan (Badshah, 1983; 1985). This complex extends beyond the limit of north Waziristan. Distinctly recognizable units of a typical ophiolite sequence do occur, however they are dismembered due to faulting. Sections showing a complete segment of the oceanic crust and upper mantle are absent (Jan et al., 1985).

The igneous rocks of the Waziristan ophiolite complex are, however, named as Waziristan igneous complex by Ahmad et al., 1987. On the basis of mineral chemistry they have suggested that the igneous rocks (ultramafic to acidic) of the complex show island arc affinity. The presence of calc-alkaline rocks have been reported by Jan et al. (1983). Hamidullah (1994)_has also suggested the existence of island arc in Waziristan area on the basis of whole rock major element chemistry.

The detail investigations are, therefore, required to differentiate the ophiolitic and calc-alkaline sequences and also to mark their extent in the region.

Igneous Rocks

The ultramafic members include harzbergite, dunite and pyroxenite. Serpentinization is common feature of harzbergite and dunite where about half of the rocks are converted to serpentinites. According to Jan et al. (1985) the Waziristan ultramafics belong to the harzbergite sub-type of Jackson and Thayer (1972). A comparison with ultramafics of the Zhob valley (Bilgrami, 1964, Ahmad and Abbas 1979) and Jijal complex (Jan and Howie 1981) is thus relevant. The ultramafic rocks are generally medium grained and commonly display deformational features and cataclastic fabrics. The harzbergite is dark-green and consist of olivine with accessory chloroenstatite and secondary serpentine, chlorite and magnetite. In the less fractured rocks olivine and pyroxene occur as relics in serpentine whereas in the intensely serpentinized rocks these are only pseudomorphs of these minerals along with ore materials. The dunites, usually formed as layer in the harzbergite, is brownish and contain chromite as sporadic accessory phase. Its predominant outcrops are near Vezhda Sar and Sherkai. Dunites are highly fractured and serpentinized. The pyroxenites dikes are composed generally of orthopyroxene with or without diopside and olivine.

The feldspathic plutonic rocks of limited extent are represented by gabbros and anorthosites. The gabbros are dull green in colour and are composed of mainly calcic-plagioclase, augite, ore minerals and in some cases olivine. Some of these rocks are quite altered with completely saussiritized plagioclase. The anorthositic rocks are composed of plagioclase with a minor amount of pyroxene and subordinate ore and olivine.

The sheeted dikes swarm is recognized at many localities but most distinct exposures are those to the north of Dattakhel and at Shuidar sar. These dikes are fine-to medium-grained, having doleritic composition and usually contain a high proportion of ferromagnesian minerals. Some of these rocks are retrograded with greenschist facies assemblage consisting of abundant actinolite/tremolite, chlorite, albitic plagioclase etc.

The volcanic rocks cover more than half of the ophiolite exposure. They are more extensively exposed towards the south where the area has not been deeply eroded. The rocks are mainly brown to green agglomerates/breccia and subordinate tuffaceous rocks. The pillow lavas have circular, oval or elongate shapes where the crust and core are easily recognizable. It is fine- grained, hard, brown to greenish brown in colour and have desert varnish on weathered surfaces. The core is coarse-grained and basaltic in composition. These lavas are mostly porphyritic and intergranular in texture by having mainly labradoritic-plagioclase and clinopyroxene. These are also intruded by the white colour dikes of variable thickness and length along which the copper mineralization is commonly associated. These dikes have not been studied in detail but some of them are trondhjemitic and essentially composed of sodic-plagioclase and quartz (for detail see Khan et al., 1982; Badshah, 1983; Jan et al., 1983; 1985). The copper minerslization, hosted by the volcanics, has been suggested as of volcanogenic massive sulfide type (Mian, I. & Afridi, 1994; Wang, 1996)

Pelagic sediments:

The upper most part of an idealized ophiolitic melange is marked by a comparatively thin veneer of pelagic sediments. In Waziristan, this unit (cherty shale "Jasperite/metachert" and limestone) has been found overlying various ophiolitic members in general and volcanics in particular with mostly tectonic contacts (Khan et al., 1982). Mappable exposures of this unit have been noticed at Serkonr, Suidar, Spinleai, Saidgi and Tut Narai areas.

The metachert/jasperite is of considerable thickness (ranges from few meters to 100 of meters). Mostly it is brown in colour and shows desert varnish and giving it a pseudo-metallic appearance. These metacherts/jasperites are embodying manganese mineralization at some places. Manganese mineralization is mostly restricted to the contact zone between the volcanic flows and the cherts and limestone in the form of lenses, veins and stringers. Structurally these cherts are very disturbed. These are thin bedded and small folding and faulting are very common.

Limestone is also common and persistent member of this unit. It is dirty gray and reddish in colour and frequently argillaceous in composition. It is generally fine-grained with poorly preserved undiagnostic fossil remains. At places desert varnish is found on the limestone surfaces due to the oxidation and weathering effect of the iron impurities. Irregular calcite veins and drag folding are common through out this member.

Unlike the typical ophiolite sequences, where the pelagic sediments overlie the basaltic flow, in Waziristan area due to extensive dismemberment of ophiolites these sediments overlie various ophiolitic units including the ultramafics through tectonic contacts.

Eocene rocks:

Most of the exposure of Eocene rocks found in un-accessible parts of the agency just west and north west of Dattakhel post, and along Tochi river. These rocks are dominantly comprised of limestone and shale members. The limestone is white in colour, fine-grained and medium-to thick-bedded. It is richly fossiliferous with forams. Limestone forms the upper part of the formation and lies conformably over the shale unit. The shale shows various shades of red and green colour and is comparatively soft and friable. It forms an almost persistent band below the limestone and above the volcanics. The contact of shale with the underlying volcanics is unconformable.

Quaternary deposits:

Quaternary deposits occur as heterogeneous materials ranging in size from boulders and cobbles to fine sand and silt form terraces, piedmonts, alluvial fans, gravel beds, channel deposits and recent alluvium in the region. These deposits normally occupy the hillslopes, valleys and the plains adjacent to and along the Tochi river and its tributary streams and seasonal water courses.

CHAPTER-3

LOCAL GEOLOGICAL SETTING

The study area (Saidgi and Shuidar) is a part of the Waziristan ophiolite complex and is mainly comprised of ultramafics, metavolcanics (pillow lavas), metachert and limestone (Fig. 2a&b). The contacts between various rock units are sharp and are considered to be tectonic in nature. No stratigraphic correlation can be made because of intense folding, faulting and exotic nature of the rocks in study area. The area can, therefore, be classified as melange zone.

ULTRAMAFIC ROCKS

In both Saidgi and Shuidar areas ultramafic rocks include harzburgites, pyroxenites, dunites, peridotites and serpentinites. These rocks are dark-green in colour and are intensely sheared and weathered at places. These rocks are generally serpentinized and contain network of microveins of white colour material (carbonates, magnesite and serpentine etc.). These rocks have chromite in the form of dissemination and also as small pods (2-4cm across). The peridotites are dark coloured and coarse-grained rocks and are mainly composed of olivine with subordinate amount of clinopyroxene and orthopyroxene.

Dunite occurs as patches within harzburgites. These are coarse-grained, dull green to brownish gray colour rocks and are mainly composed of olivine, with minor pyroxene. It has typical reddish-brown alteration surface. Stringers and veins of chromite are rarely observed. Harzburgites are more common than the rest of the ultramafics. These are coarse-grained, dark-green to black colour rock. Individual crystal of orthopyroxene exhibit a micaceous luster.

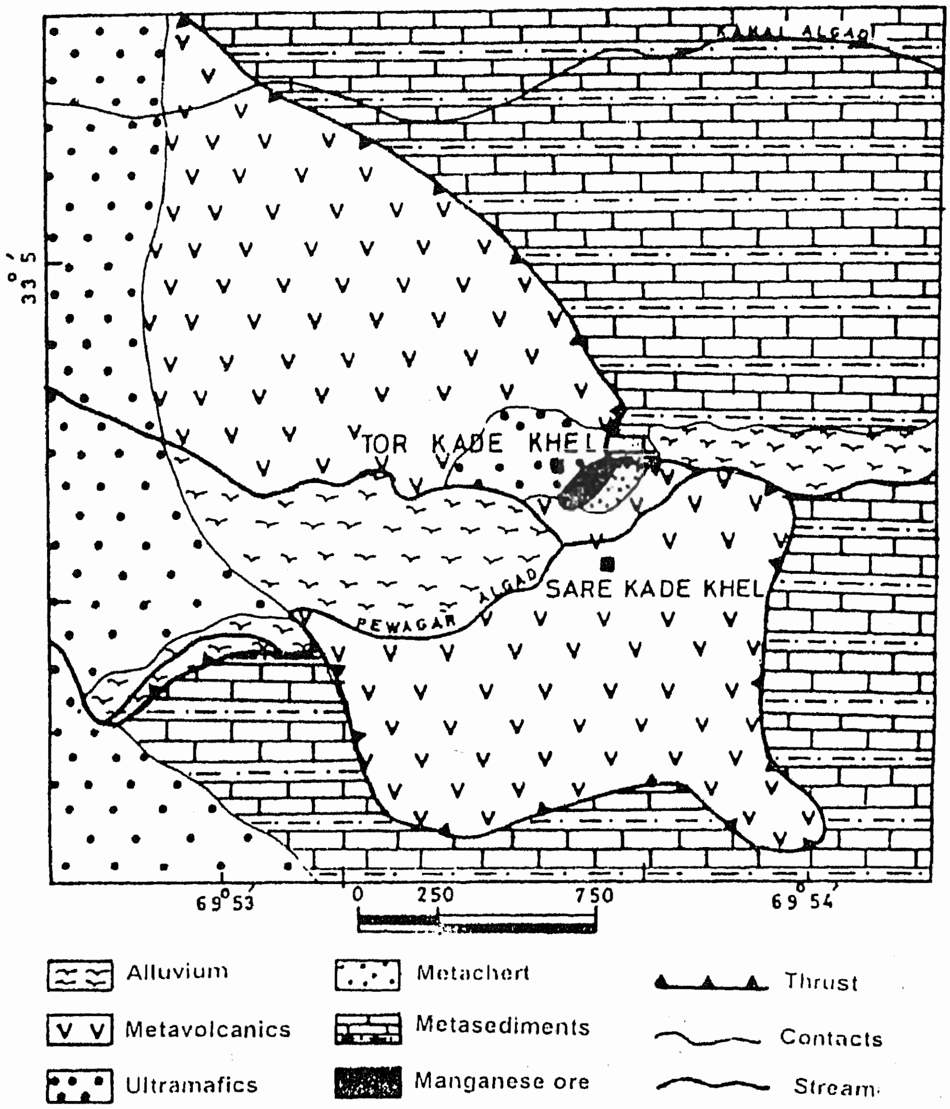


Fig. 2a. Geological map of the Saidgi area, north Waziristan.

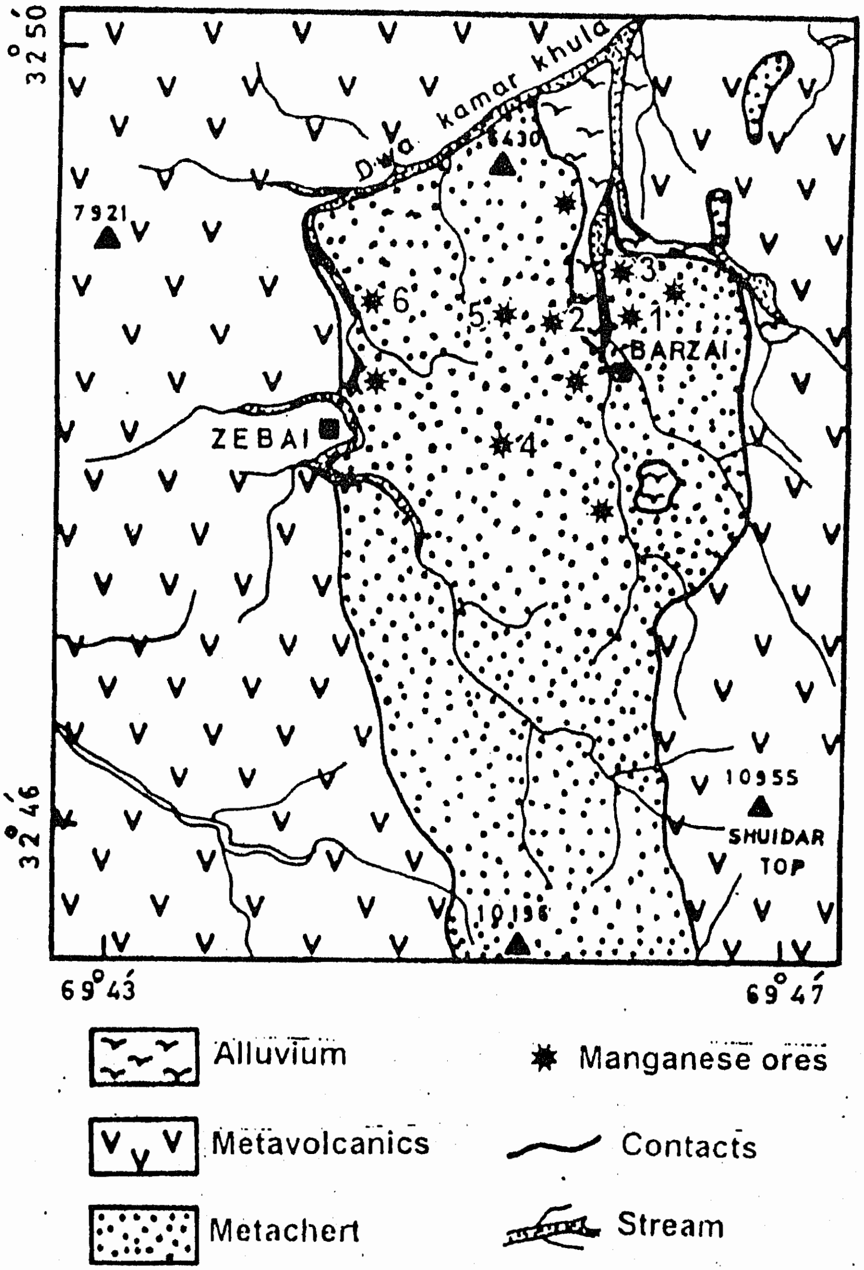


Fig. 2b. Geological map of the Shuidar area, north Waziristan.

Olivine and orthopyroxene are the main constituents with minor clinopyroxene. Alteration has caused development of serpentine, talc and chlorite at places

Pyroxenites in the area are dark green and coarsely crystalline. Clinopyroxene and othopyroxene are the main phases with minor amount of plagioclase. At places these minerals are partially or completely altered to serpentine, talc, chlorite, carbonates, kaoline. In the highly tectonized parts development of magnesite becomes more conspicuous.

METAVOLCANIC

The metavolcanics occur as voluminous lava flows, with pillow structures at places, in both Saidgi and Shuidar areas. These are generally found in association with the manganese deposits and metacherts. At places these also show pyroclastic brecciated nature having clasts ranging in size from 1cm to 3cm in length. Most of the clasts are elliptical to rounded and could be termed as matrix supported breccia. The clasts have porphyritic texture with plagioclase and pyroxenee phenocrysts. The plagioclase phenocrysts are generally altered to clay material. The pillow structures on the surface of these metavolcanics are found adjacent to the Mn-deposits and metacherts. These lavas have gasseous pits which are filled in by the carbonates. At places the metachert and limestone are incorporated into these lavas and have chilled margins against them. These volcanics are highly sheared and schistosed along the shear zones where these appear as greenschist and have developed greater concentration of chlorite.

In thin sections these rocks have basaltic to basaltic-andesite composition having porphyritic to subporphyritic vesicular texture. The phenocrysts are made up of rarely zoned pyroxene and plagioclase. The groundmass consist of plagioclase, pyroxene, chlorite, epidote, sericite and ore minerals. Microveins of calcite and quartz are also noticed.

METACHERTS

The metcherts are finely crystalline, thin to medium bedded, hard rocks of dull reddish brown to maroon colour (plate 1-6). In both Saidgi and Shuidar areas the metachert overlies the metavolcanics. These have an average thickness of ~100m at Saidgi and ~2000m at Shuidar. In Saidgi area these cherts have greenish gray colour (up to about 1m) at the contact of metavolcanics and then attain maroon colour. This indicates the gradational contact of metacherts with the lower lying metavolcanics.

The metachert contains more than 70% non-detrital free silica and consisting mainly of fine cryptocrystalline quartz and a minor clay fraction. At places the metachert has pseudomorphs of radiolarian tests which are now filled in by detrital quartz and calys.

MANGANESE ORE BODIES

In both Saidgi and Shuidar area the manganese deposits are banded and massive in nature. (plate 1-5). These deposits do not differ significantly in mineralogy, but only in structural and textural character. The manganese ore bodies in Shuidar area are generally banded in nature. These banded ore bodies consist of Mn rich layers alternating with layers of metachert. These layers of metacherts by themselves are having thin (<1cm) bands of Mn-minerals. The ore bodies lie at a variable distance from metavocanics-metacherts contact. In Saidgi area the Mn-ore bodies are generally massive in character. The massive ore bodies occur in the form of lenses (~6m thick and ~60m long). These ore bodies are contained within less than 50m from metavolcanics-metacherts contact.

METASEDIMENTS

Metasedimentary unit of the Indian plate is dominantly exposed in the eastern part of the Saidgi area. It occurs as a thick sequence of limestone Shale and sandstone and has thrusted contact with the metavolcanics in the area (Fig 2a) Limestone is dark gray in clour and is interbedded with black to brown shale and gray to light gray sandstone. The sandstone occassionally exhibit Fe and Mn coating at the weathered surface. Recumbent and cheveron type macro and micro-folding is the prominert feaure of these rocks which is indicative of existance of the major thrust in the area.

Llimestone also occurs in the form of pockets and lenses within the metavolcanics in Saidgai and Shuidar areas .This type of limestone is light grey to cream in colour and is richly fossiliferous. On the basis of the presence of fossils an age of early Eocene is assigned to this limestone(Badshah, 1985).

Plate 1. A view of the contact between low-lying metachert (Maroon color) and the upper-lying massive Mn-ore body (black color) in Saidgi area.

Plate 2. A view of the metachert and hosted massive Mn-ore body in Saidgi area. The metachert is also enclosed within the Mn-ore body.

Plate 3. Another view of the Mn-ore body of Saidgi area. Here the contact between lower lying metavolcanics, thinly bedded metachert and thinly bedded to massive Mn-ore body is very clear.

Plate 4. Another view of the Mn-ore body of Saidgi area from southern side where the massive Mn-ore bodies are enclosed within the metachert.

Plate 5. Photograph showing the thinly bedded (Stratiform) nature of both Mn-ores (black-gray color) and metachert (maroon color) in Shuidar area.

Plate 6. Photograph showing the banded and fractured nature of metacherts in Shuidar area.

CHAPTER-4

LITERATURE REVIEW ON MANGANESE DEPOSITS

HISTORY

Manganese is an essential component of the steel and cast-iron making industry and, therefore, has greater importance from the industrial point of view. It mainly occurs as oxides and hydroxides in the earth crust. Manganese oxide was considered as a variety of iron and was used by the ancient Egyptians and Romans for controlling the colour of glass and pottery until the latter part of the 18th century. Manganese ores were consumed extensively in the production of Chlorine (Harder, 1910). Umber, a mixture of manganese and iron oxides, has been reported as a drier for oils as early as the middle of 17th century (Lavino, 1960). The first record of mining of manganese ore in the United States was in 1837 in Hickman County, Tennessee., apparently for the purpose of colouring earthenware.

Robert Mushet introduced manganese in the form of spiegeleisen. Since then, manganese has been necessary to the commercial productions of all steels. Ferromanganese, cantaining 25 to 30 percent manganese was first produced for commercial use in 1865 by Henderson, followed closely by Pricger, who produced an alloy with 75% manganese. The Terre Noire company improved these earlier processes and started for the first time the production of rich and cheap ferromanganese (Harder, 1910).

TYPES OF MANGANESE DEPOSITS

Geologically manganese deposits are of various types. These could be sedimentary, metamorphic, lateritic, and hydrothermal deposits. Underwater manganese deposits range from the small oxide deposits of bogs to the very extensive deposits of oxide nodules and encrustations that are currently the subject of such investigation on the deep ocean floors.

In addition, there are unique manganiferous metalliferous muds in the depths of the Red sea.

Manganese deposits of different geological ages are formed as chemical sediments in a variety of tectonic and geo-chemical environments. During Precambrian the geosynclinal deposits were common while the platform type of deposits were common during Phanerozoic. The sources of these manganese-rich sediments were either the weathering zone on the continent or direct (mainly submarine) volcanism of both basic and acidic type and also the hydrothermal processes. These are, therefore, divided into two main types a) hydrothermal & b) Sedimentary (Roy, 1976, 1981,1992). The hydrothermal deposits are smaller in size as compared to that of sedimentary deposits. Traditionally the sedimentary deposits have been classified as volcanogenic (or exhalative) and non-volcanogenic (terrigenous) types, based on the presence of volcanic rocks in vicinity or distal areas. These can not be distinguished from the modern sediment-hosted hydrothermal Mn-deposits at or near the ocean spreading centres and in island arcs (Roy, 1992). Nicholson (1992), however, classified the manganese oxide deposits as supergene and hydrothermal on the basis of formation processes and depositional environments. The supergene deposits have further been divided into terrestrial (bogs & soily fresh water, weathering & dubhites) and marine (crust, coatings, Nodules, sediments) while the hydrothermal as terrestrial (hotspring & veins) and marine (sedimentary exhalative). The deposits that were formed from a non-volcanogenic source may either be geosynclinal or platform-type and are characteristically associated with terrigenous formation (argillaceous rocks), carbonate formation (limestone & dolomite) and iron formation. Volcanogenic-sedimentary manganese deposits are mainly geosynclinal and rarely of platform type and belong to green stone-siliceous (with basic volcanic & subvolcanic rocks) and porphyry-siliceous (with acid volcanic and subvolcanic rocks) groups in which the manganese deposits are either associated directly with basic or acidic volcanic or sub-volcanic rocks or with chert, Jasper and siliceous shales or carbonate.

Fresh water ferro-manganese deposits occur in lakes and streams that occupy local and regional depressions in glaciated terrains. Two major sources of dissolved metal appear important in the development of fresh water ferro manganese concentrations: a) lake and river water overlying the nodule substrate, and b) interstitial water/ground water percolating through the substrate. Aqueous solutions containing iron, manganese, and other less abundant transitional metals encounter suitable nuclei in an oxidizing environment, where ferro manganese oxides of varying Fe/Mn ratios and minor metals contents precipitates.

Deep-sea manganese nodules, occur on the surface of ocean floor, can be formed by different ways: a) The manganese of the nodules is chiefly derived from the decomposition of the more basic volcanic rocks and minerals with which the nodules are nearly and always associated in deep sea deposits, b) They are formed under the reducing influence of organic matters on the sulfides being produced and subsequently oxidized c) They rise from the precipitation of manganese contained in the waters of submarine exhalations at the bottom of ocean, and d) They are formed from the compounds of manganese dissolved in sea water in the form of bicarbonates, and transformed at the surface of the sea into oxides, which are precipitated in a permanent form on the bottom of the ocean.

MINERALOGY OF MANGANESE DEPOSITS

Many of the problems regarding manganese and manganese bearing phases and their genesis have been resolved now, however, the mineralogy of many phases had not been worked out even today. The manganese minerals are present as oxides, hydroxides, carbonates silicates, sulfides, and the more rarely occurring arsenates, arsenites, phosphates etc. Primarily the oxides and hydroxides form the ore deposits and the carbonates are considered as protore. Manganese minerals of other compositions are usually not considered as forming ore bodies.

Oxides constitute the most important manganese ore minerals. Physically they grade from quite hard and dense to friable and earthy. Many are of secondary origin, formed under the influence of weathering.

More than 40 manganese minerals have been identified so far. Among these the most important are: Birnessite [$(Ca\ Na)\ (Mn^{+2}\ Mn^{+4})\ O_{14}.\ 3H_2O$], Braunite [$Mn,^{+2}Mn_6^{+3}O_8(SiO_4)$], chalcophanite [$Zn\ Mn_3^{+4}\ O_7.3H_2O$], Crednerite[$Cu\ MnO_2$], Pyrolusite[$MnO_2$], Nsutite [$MnO_2$], Cryptomelane[$K\ Mn_8O_{16}.\ H_2O$], HausMannite [$Mn^{+2}\ Mn_2^{+3}O_4$], Jacobsite [$Mn\ Fe_2O_4$], Pyrochoite [$Mn(OH)_2$], Pyrophanite [Mn TiO3], Ramsdellite [MnO^2], Manganite [MnOOH], Hollandite [$(Ba,K)_{1\text{-}2}\ Mn_8O_{16}.H_2O$].

ENVIRONMENT OF FORMATION OF MANGANESE OXIDE MINERALS BY NICHOLSON 1992

Nicholson (1992) has given slightly different classification scheme for the formation of manganese oxides as compared to that of Roy (1981) & (1992). He has classified the Manganese oxide deposits as "supergene" and "hydrothermal" by considering first the mineral forming processes are subdivided into terrestrial and marine type. Nicholson (1992) used the term "supergene" for those oxides which are formed under ambient conditions at the earth surface in both terrestrial and marine environment and not only restricted to the secondary enrichment of Mn-oxide as Roy 1981 & 1992 suggested. The proposed classification of Nicholson, 1992 is briefly described here.

A) Supergene Terrestrial deposits:

This include mainly a) Bogs soils, b) fresh water c) weathering and d) dubhites deposits.

a) Bogs and soils: All accumulations of manganese oxides formed in the soil profiles, including swamps or bog deposits, regardless of morphology i.e. crust coatings, nodules etc.

b) Fresh water deposits: Cements and coatings on steam or lacustrine sediments, lacustrine nodules, lacustrine sediments, oxide coatings and vein deposited from ground water.

c) Weathering deposits: Surface crusts and coatings formed by weathering, dendrites, desert varnish, laterites etc.

d) Dubhites: Oxides formed by the weathering of mineralized sequence (from the Gaelic dubhithir "black earth", & gossan "ferruginous earth") i.e. the manganese oxide equivalent of a gossan.

B) Supergene marine deposits:

This include manganese nodules, crusts and coatings which are precipitated directly from sea water (hydrogenic-hydrogenous deposits) and bedded manganifesous sediments deposited in the marine environment with the manganese supplied from sources other than hydrothermal (i.e. continental run-off, hydrogenic, digenetic, halmyrolytic). In some cases the shallow-marine deposits are differentiation from deep marine or deep sea Mn-oxide deposits.

A) Hydrothermal terrestrial deposits:

These type of deposits include hot spring and veins.

a) Hot springs: These are the deposits which are formed directly from geothermal waters around hot springs and pools.

b) Veins: This includes only the primary precipitates and not the minerals in the upper oxidized sequence.

B) Hydrothermal marine deposits: These deposits are mainly the bedded or stratiform manganiferous sediments of exhalative origin.

CHAPTER - 5

PETROGRAPHY / MINERALOGY

MANGANESE DEPOSITS

Mineralogical studies were carried out by the microscopic investigations of polished thin sections using both polarizing and reflectance Nickon microscope. X-ray diffraction analyses were carried out by using Rigaco X-ray Diffractometer. Mineral analyses were carried out by using Electron microprobe. All these studies were performed at the National Centre of Excellence in Geology, University of Peshawar.

Many of the samples of manganese ore bodies from both Saidgi and Shuidar area are having mixtures of quartz and braunite (Plate 7-10). The pseudomorphs of radiolarian tests (Plate 11) are also visible within the matrix. No other manganese minerals are identified in these ores. Quartz occurs as cryptocrystalline grains associated with braunite and hematite and is the second most frequent constituent of the studied ores. It also occurs as microveins. The Shuidar Mn-deposits, however, have hematite in addition to braunite and quartz. Hematite generally occurs as dissemination in these ores (Plate 12). It is because of the presence of hematite that the bulk rock chemistry shows high concentration of iron in Shuidar Mn-deposits relative to that of Saidgi.

Braunite is ranging from microcrystalline to euhedral in shape. The microcrystalline braunite is intermixed with microcrystalline to cryptocrystalline quartz while the coarse grained braunites are interlocked with each other and are occasionally crosscut by microveins of quartz. The ideal composition of natural braunite is Mn_2O_3. Mn SiO_3, corresponding to about 10% SiO_2 by weight (Palache et al., 1944). The microprobe analyses of braunite (Table 1) suggest that the studied braunite conforms reasonably well to this formula as of having SiO_2 (up to 11.40%), MnO (up to 87.06%) and CaO (up to 1.65%) while rest of the oxides (i.e. TiO_2, FeO & MgO) are less than 0.50 wt%. The studied braunite is, however, very low in iron (<0.20 wt%) as compared to the other braunite reported elsewhere (Table 1). The studied braunite has more or less similar

Table 1. Chemical analyses of braunite from Saidgi and Shuidar area, north Waziristan and its comparison with the other braunite analyses elsewhere in the world.

S.No.	WSM58	WSM78	BT3C	DKT1B	1	2	3	4
SiO_2	11.40	11.06	11.13	11.36	10.30	9.32	10.26	9.80
TiO_2	0.04	0.00	0.00	0.00	0.05	0.00	0.00	0.00
Al_2O_3	0.28	0.11	0.25	0.54	0.35			1.40
Fe_2O_3	--	--	--	--	0.34	1.44	1.59	6.20
FeO	0.20*	0.17*	0.18*	0.12*	--			--
Mn_2O_3	--	--	--	--	--	--	--	--
MnO	85.59	86.21	87.07	86.82	8.58	86.60	78.91	77.50**
MgO	0.07	0.00	0.11	0.08	B.D.	0.00	4.36	--
CaO	1.32	1.35	1.44	1.65	1.52	--	--	--

* = Total iron expressed as FeO

** = Total manganese expressed as MnO_2

B.D.= Below dectection limit

1 = Braunite from Postmasburg, S. Africa (Gutzmer and Beukes, 1997)

2 = Braunite from Kalahari, S. Africa (De villier, 1945)

3 = Braunite from Kajlidongri, India (Fermor, 1909)

4 = Braunite from Groote Eylandt, Australia (Ostwald, 1982)

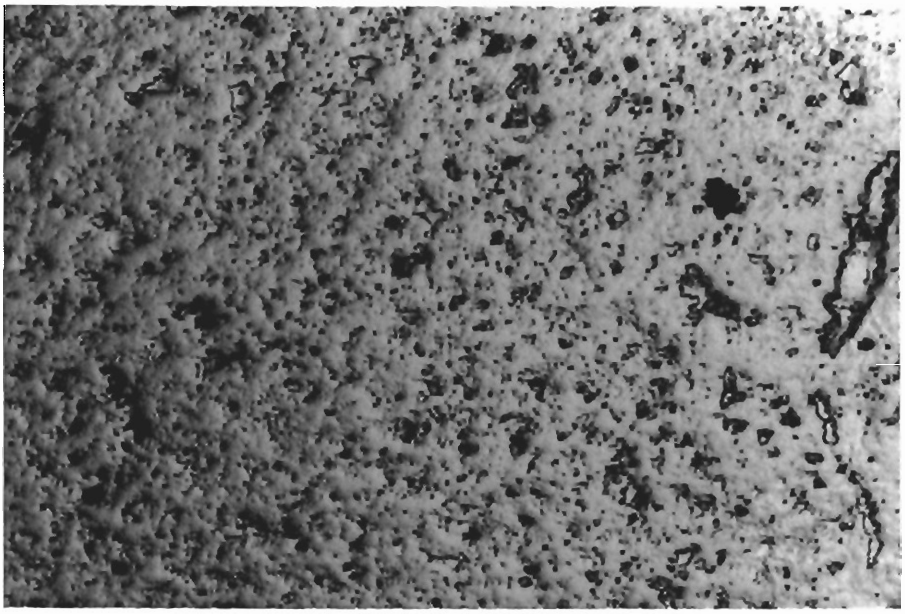


Plate 7. Photomicrograph showing a view of the braunite in the Mn-ores of Saidgi area in reflected light. It is giving light grey reflectance. The whole view is covered by bruanite grain. spots and pits area due to bad polished surface (X4).

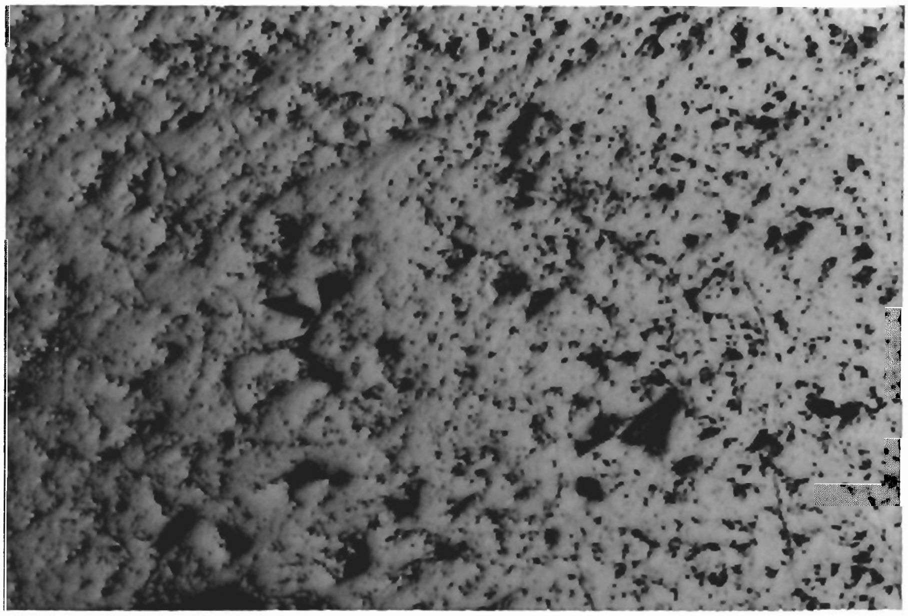


Plate 8. Photomicrograph showing braunite of Shuidar area in the reflected light. It is same as of Saidgi area (X4).

Plate 9. Photomicrograph showing braunite (black color) enclosing the cryptocrystalline quartz (chert) in the Mn-ores of Shuidar area in cross light (X4).

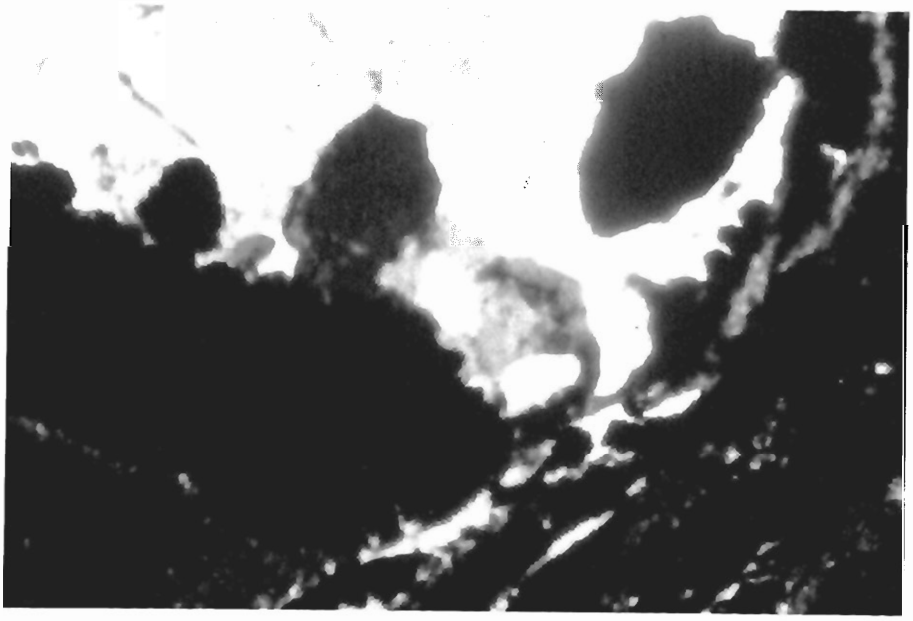


Plate 10. Photomicrgraph showing medium grained interlocked grains of recrystallized quartz in the form of patches within braunite (black color) in the Mn-ores of Saidgi area (X4).

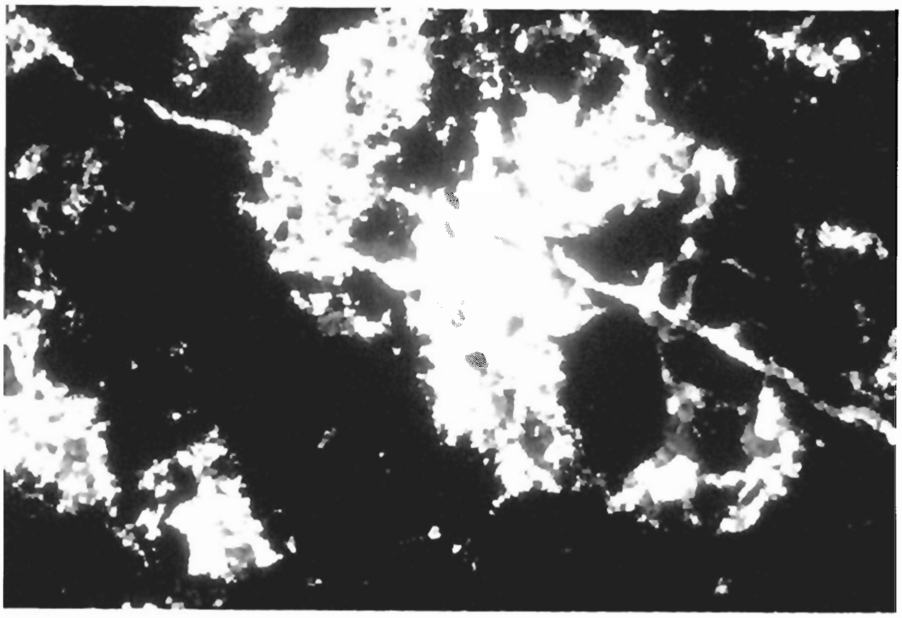
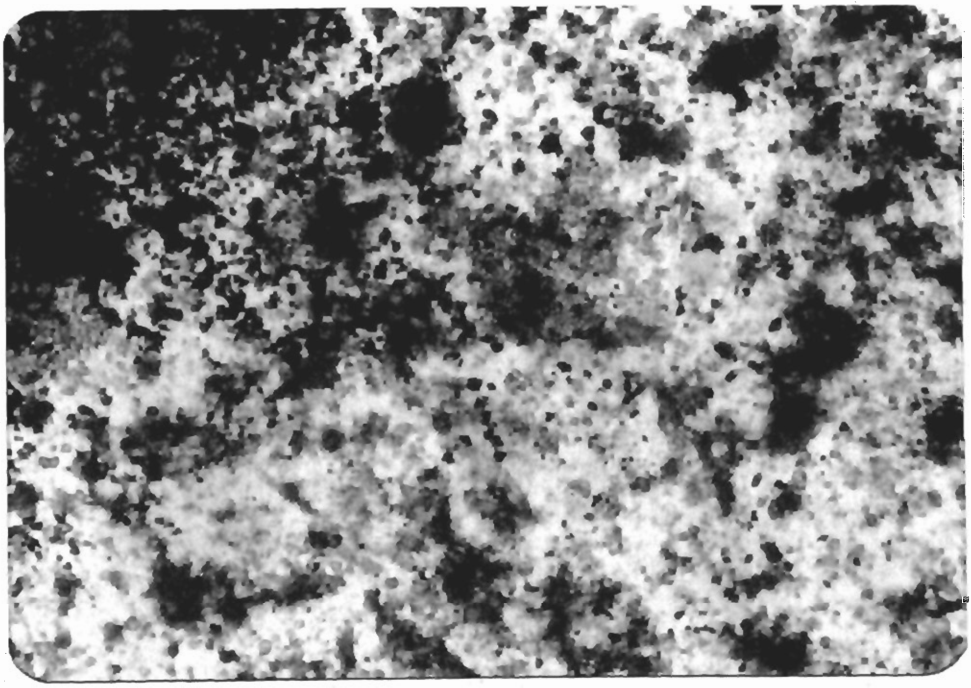


Plate 11. Microphotograph showing pseudomorphs of rounded to sub-rounded radiolarian tests which are now replaced by the cryptocrystalline quartz enclosed within braunite in Mn-ore samples of Saidgi area. The micro veins of quartz are also visible (X2.5).



late 12. Photomicrograph showing hematite matrix (reddish color) and the cryptocrystalline quartz in plane light in the Mn ore of Shuidar area (X4).

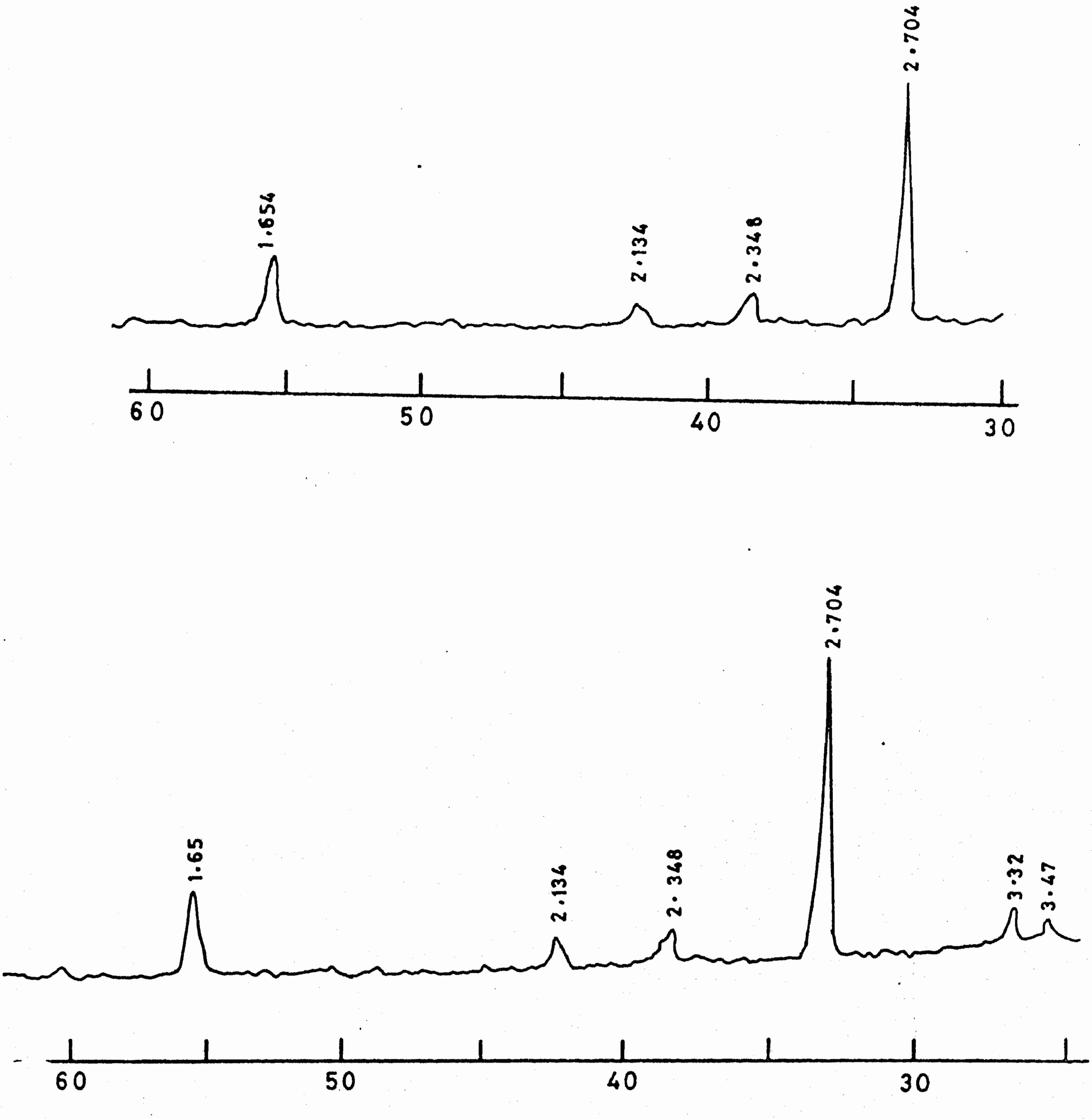


Fig.3. X-ray diffraction pattern for the braunites from the Mn-deposits of Saidgi and Shuidar areas.

composition to that of S. Africa (Table 1) and has high MnO and less MgO and TiO_2 as compared to that of India (Table 1). The powder X-ray diffraction pattern of the studied braunite along with D spacing are given in Figure 3. These are also consistent with the natural barunite.

Braunite is best known from its occurrences in the Apennine ophiolites (Bonatti et al., 1976) in regionally metamorphosed manganese deposits (Roy, 1981), in hydrothermal veins (Frenzel, 1980), in unmetamorphosed sediments (De La Hunty, 1963) and sedimentary manganese ores of Sabkha-type in Groote Eylandt, Australia (Ostwald, 1982).

According to Bonatti et al. (1976) the present day manganese deposits of the ocean floor are lacking braunite. However, they have reported braunite as the dominant Mn-bearing phase in the metalliferous deposits of Apennine ophiolites. The formation of Braunite in the ophiolites and other metamorphic terrain can be considered as postdepositional phenomenon where the Mn-minerals have reacted with the silica (associated chart) during mild metamorphism either at the time when ophiolites were still the part of oceanic crust or during and (or) after the obduction of ophiolites (Bonatti et al., 1976; Choi & Hariya, 1992; Sakakibara, 1986). Their interpretation is consistent with the fact that braunite is stable up to moderately high temperature as it has been synthesized in the laboratory at high temperature (Muan, 1959a, 1959b) and it also occurs in metamorphosed Mn-deposits (Palache et al., 1976).

This suggest that the presence of braunite in the studied ore bodies can be considered as an indication of the existence of these Mn-deposits in an ophiolitic sequence.

METACHERTS

The metacherts of both Saidgi and Shuidar areas have the similar field and mineralogical characteristics and are, therefore, described together. The metacherts are exceedingly microcrystalline aggregates. These are mainly composed of microcrystalline quartz, chalcedony and lesser hematite (Plate 13 & 14). Rounded to oval shaped pseudomorphs of radiolarian are also noticed. Those are replaced by quartz, in a matrix of microcrystalline quartz chalcedony and hematite. At places carbonate and clay minerals disseminations have also been noticed.

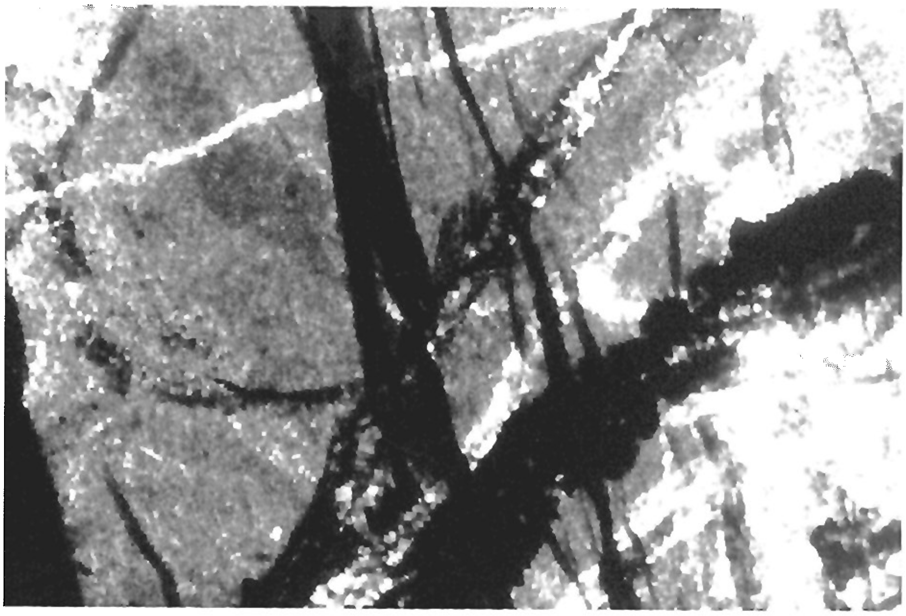


Plate 13. Microphotograph showing chert / chalcedony (grey color) as a main phase having fractured filled braunite (reddish black) and crytocrystalline quartz (light color) in cross light within the Mn-ores of Shuidar area (X4).

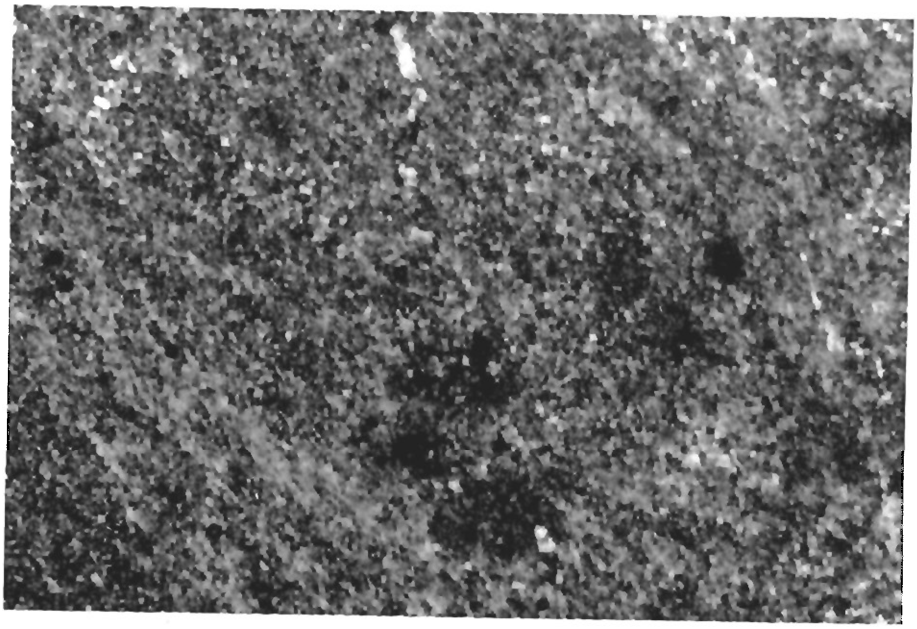


Plate 14. Photomicrograph showing metachert, having cryptocrystalline quartz and clay material, in cross light (X2.5).

CHAPTER- 6

GEOCHEMISTRY

MANGANESE DEPOSITS

Major elements

The chemical composition of both Mn-deposits of Saidgi and Shuidar are presented in Table 2. This table shows that the Saidgi deposits have SiO_2 ranging from 31.67 to 58.79 wt%, MnO from 36.72 to 60.56 wt%, MgO from 0.09 to 1.16 wt%, CaO from 0.10 to 3.45 wt% Al_2O_3 from 0.42 to 0.88 wt%, Fe_2O_3 from 0.08 to 2.43 wt%, Na_2O from 0.06 to 0.79 wt%, K_2O from 0.03 to 0.73 wt%, TiO_2 from 0.05 to 0.40 wt% and P_2O_5 from 0.03 to 0.45 wt%. These samples also have high ignition loss (up to 9%).

The Shuidar deposits have low MnO (25.73 - 46.34 wt%) and high Fe_2O_3 (2.50 - 15.53 wt%) as compared to Saidgi deposits. The rest of the oxides such as SiO2 (42.34 - 57.40 wt%), TiO_2 (0.10 - 0.62 wt%), Al_2O_3 (0.49 - 1.23 wt%), MgO (0.02 to 1.14 wt%), CaO (0.15 - 1.96 wt%), Na_2O (0.06 - 0.67 wt%), K_2O (0.03 to 1.58 wt%), and P_2O_5 (0.02 to 0.52 wt%) are more or less similar to that of Saidgi deposits. These deposits also have relatively less ignition loss (0.75 - 4.62).

Various major oxides are plotted against MnO in Figure 4 in order to see their mutual correlation. SiO_2, Fe_2O_3, Al_2O_3 and TiO_2 show vaguely defined negative correlation against MnO while MgO, CaO, Na_2O and P_2O_5 have scattering of data and, therefore, exhibit no correlation with MnO (Fig. 4).

Table2. Chemical composition of Mn-deposits of Saidgi and Shuidar areas, north Waziristan.

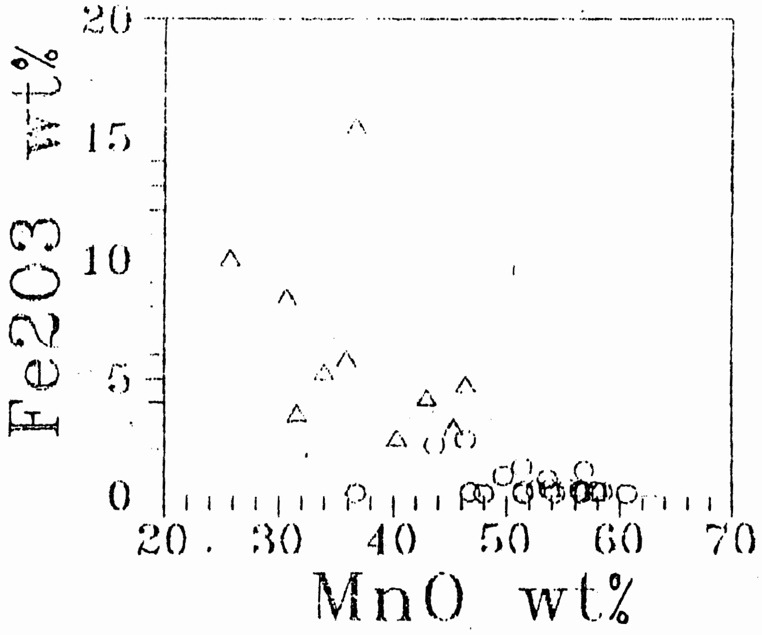
SAIDGAI S.No.	WSM1	WSM7	WSM13	WSM21	WSM23	WSM26	WSM28	WSM29	WSM33	WSM39
SiO_2	42.78	36.45	34.78	50.21	40.97	36.56	34.89	37.78	38.12	35.78
TiO_2	0.32	0.40	0.26	0.23	0.31	0.16	0.13	0.32	0.21	0.30
Al_2O_3	0.78	0.85	0.65	0.61	0.78	0.54	0.53	0.76	0.62	0.68
Fe_2O_3	0.85	0.25	0.22	2.19	1.23	0.30	0.28	0.07	0.23	0.09
MnO	49.67	56.45	57.78	43.67	51.32	55.34	53.78	47.98	56.54	54.23
MgO	0.70	1.05	0.62	0.51	0.85	0.79	0.79	0.50	0.94	0.79
CaO	0.75	0.94	0.83	0.21	0.10	1.99	3.01	3.45	0.84	1.83
Na_2O	0.58	0.10	0.52	0.06	0.26	0.06	0.72	0.69	0.12	0.74
K_2O	0.36	0.07	0.09	0.03	0.73	0.20	0.16	0.23	0.05	0.07
P_2O_5	0.14	0.17	0.26	0.27	0.45	0.41	0.18	0.21	0.05	0.06
L.I.O	2.48	4.04	2.70	0.90	1.57	4.00	5.25	7.86	1.92	3.96
Total	99.41	100.77	98.71	98.89	98.57	100.35	99.72	99.85	99.64	98.53
Trace elements in ppm										
Cu	42	48	34	24	25	22	31	24	125	35
Pb	44	27	40	42	38	54	72	64	26	34
Zn	24	67	42	14	18	38	26	30	31	34
Ni	42	16	24	18	16	45	0	10	14	28
Cr	39	24	89	20	36	67	12	25	28	45
Co	8	4	5	14	9	4	4	0	5	0
Fe/Mn	0.015	0.004	0.003	0.045	0.022	0.005	0.005	0.001	0.004	0.001

(Continue table2)

SHUIDAR S.No.	DKT1B	DKT4C	DKT5A	DKT13C	DKT15B	BT1A	BT3C	BT9B	BT9A	BT22A
SiO2	45.30	56.89	51.07	57.40	55.56	56.78	44.12	47.14	49.45	42.34
TiO2	0.15	0.72	0.23	0.24	0.54	0.54	0.62	0.10	0.46	0.56
Al2O3	0.53	1.23	0.65	0.67	0.91	0.94	0.99	0.48	0.83	0.88
Fe2O3	4.25	3.56	5.87	10.06	5.32	8.43	15.53	2.96	2.50	4.80
MnO	42.98	31.56	35.85	25.73	33.96	30.67	36.67	45.34	40.34	46.34
MgO	0.17	1.14	1.00	0.31	0.42	0.11	0.42	0.04	1.00	0.02
CaO	1.58	0.20	1.16	0.25	0.85	1.03	0.41	1.41	0.15	1.86
Na2O	0.07	0.22	0.13	0.10	0.11	0.21	0.07	0.07	0.67	0.06
K2O	0.23	0.14	0.17	0.12	0.21	0.06	0.19	0.05	1.58	0.03
P2O5	0.31	0.12	0.02	0.31	0.25	0.02	0.50	0.20	0.52	0.47
L.I.O	4.42	4.16	2.03	4.62	2.23	0.75	1.56	1.61	2.00	2.04
Total	99.99	99.94	98.18	99.81	100.36	99.54	101.08	99.4	99.5	99.4
Trace elements in ppm										
Cu	160	155	78	73	84	94	155	186	145	86
Pb	59	45	57	34	36	58	73	68	45	63
Zn	83	75	86	34	72	56	150	124	58	134
Ni	74	62	54	23	58	54	56	64	26	76
Cr	68	84	59	45	75	43	41	36	58	62
Co	18	15	23	34	20	32	38	17	15	23
Fe/Mn	0.089	0.102	0.148	0.353	0.141	0.248	0.382	0.059	0.056	0.094

(Continue table2)

S.No.	WSM44	WSM56	WSM58	WSM60	WSM67	WSM70	WSM78	WSM82	WSM87	WSM88
SiO2	39.56	38.67	33.98	35.76	41.78	35.78	31.67	38.45	38.45	42.34
TiO2	0.12	0.25	0.10	0.08	0.14	0.11	0.15	0.06	0.27	0.17
Al2O3	0.51	0.65	0.48	0.42	0.49	0.43	0.53	0.48	0.68	0.49
Fe2O3	0.08	0.13	0.16	0.09	0.25	0.14	1.09	0.21	0.71	2.43
MnO	51.45	46.78	57.98	56.56	52.56	56.87	56.78	51.45	53.56	46.34
MgO	0.39	0.63	0.21	0.38	0.49	0.31	0.36	1.07	1.16	0.21
CaO	2.45	3.22	1.13	2.45	1.02	1.30	3.36	1.82	1.56	0.74
Na2O	0.06	0.79	0.06	0.13	0.29	0.62	0.36	0.74	0.05	0.66
K2O	0.19	0.07	0.05	0.20	0.07	0.07	0.30	0.05	0.16	0.12
P2O5	0.20	0.25	0.42	0.13	0.03	0.14	0.04	0.26	0.22	0.13
L.I.O	4.10	8.78	3.67	4.65	2.83	3.42	4.50	7.04	2.66	5.85
Total	99.11	100.22	98.24	100.85	99.95	99.19	99.14	101.63	99.48	99.48
Trace elements in ppm										
Cu	55	32	37	64	130	55	98	87	36	23
Pb	44	64	48	64	34	52	42	48	31	36
Zn	52	37	36	19	36	45	34	43	23	38
Ni	32	35	47	34	43	41	13	36	28	14
Cr	39	56	48	53	45	58	34	49	38	23
Co	0	4	5	0	8	4	10	4	6	12
Fe/Mn	0.001	0.003	0.002	0.001	0.004	0.002	0.017	0.004	0.012	0.047



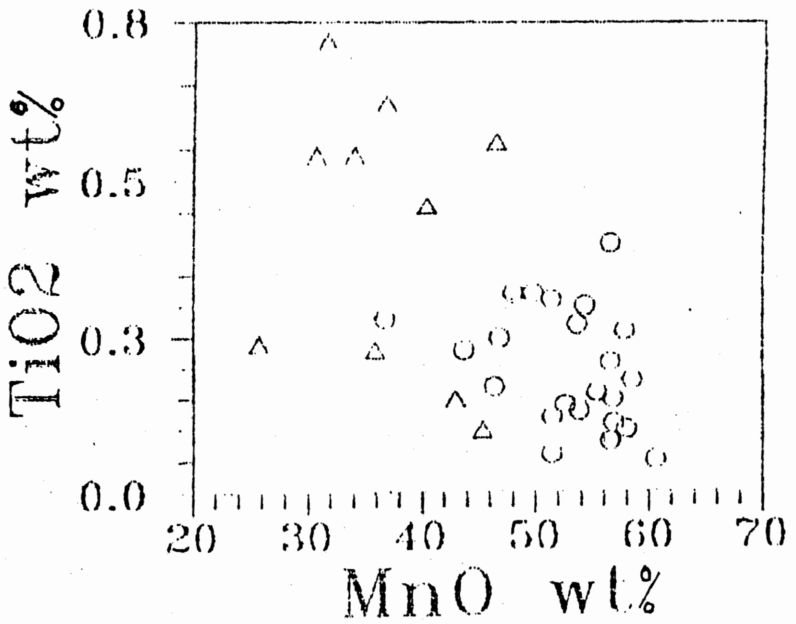
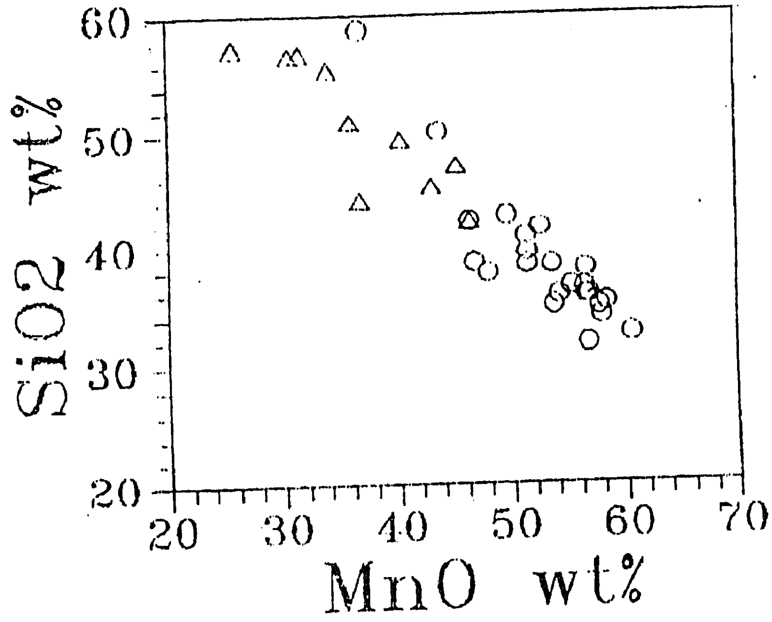
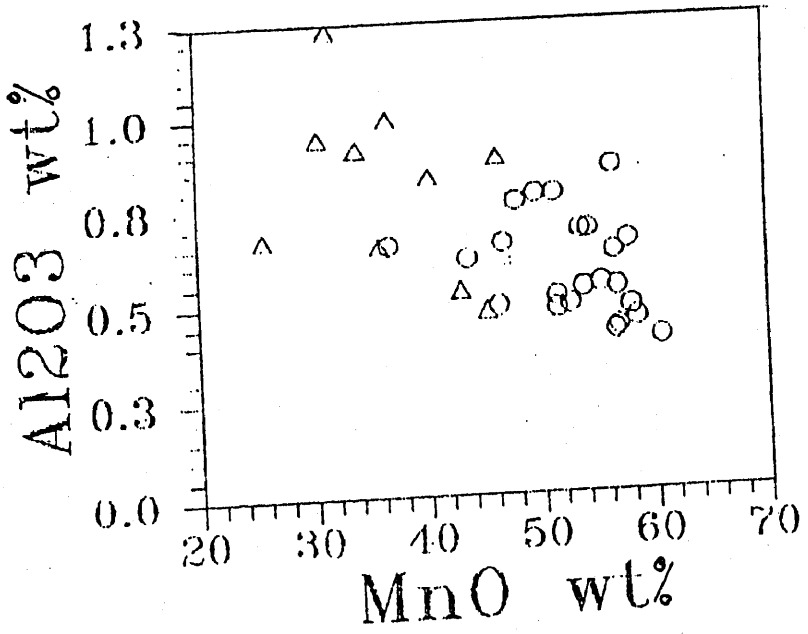
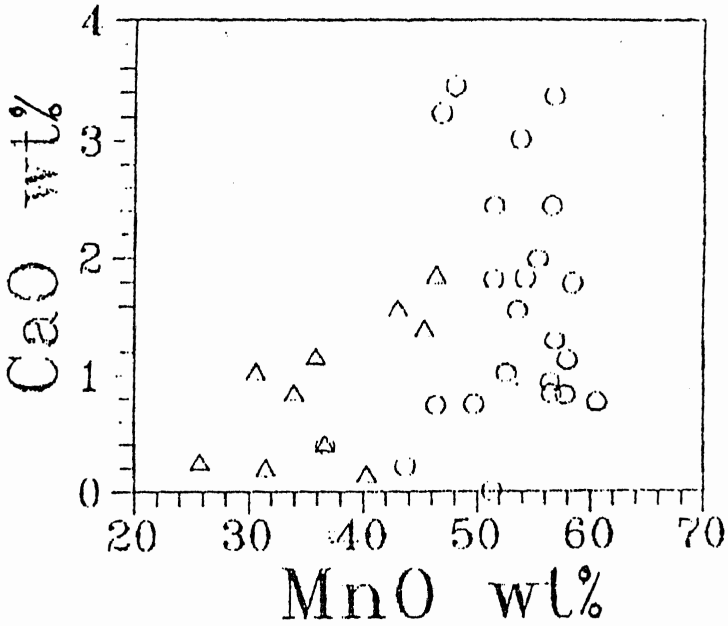


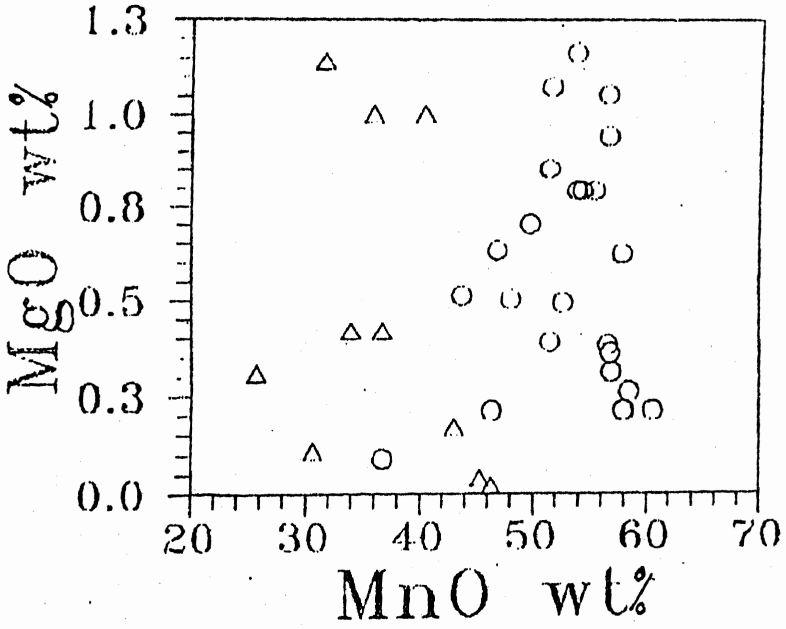
Fig. 4. Plot of Fe_2O_3, TiO_2, Al_2O_3, SiO_2, MgO, CaO, Na_2O and P_2O_5 against MnO for the Mn-deposits of Saidgi and Shuidar areas.

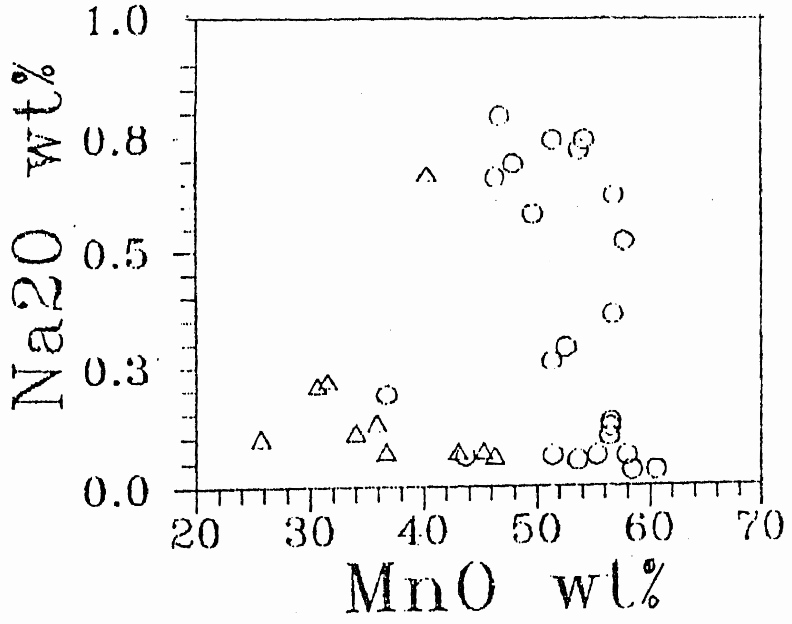
Symbols: O = Saidgi, Δ = Shuidar


SiO2 wt%
60
50
40
30
20
20
30
40
50
60
70
MnO wt%

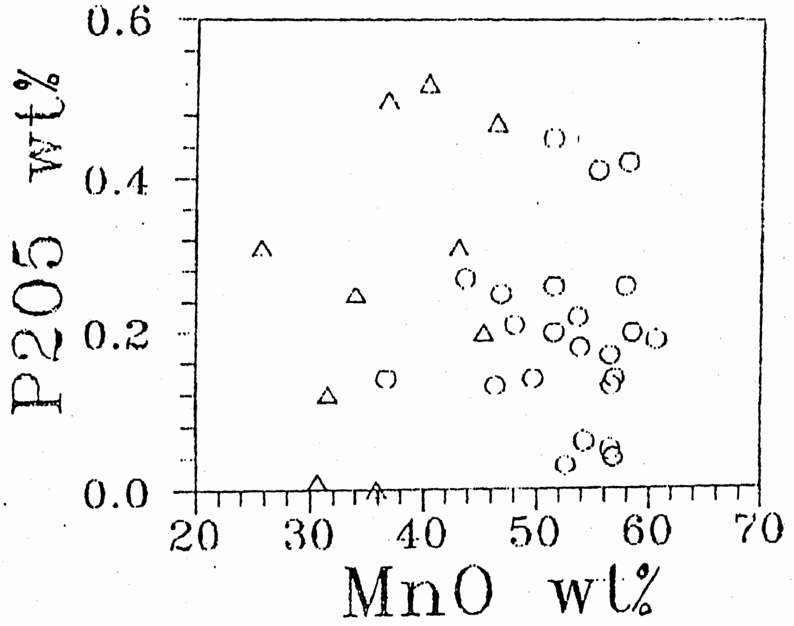

Al2O3 wt%
1.3
1.0
0.8
0.5
0.3
0.0
20
30
40
50
60
70
MnO wt%


CaO wt%
MnO wt%
0
1
2
3
4
20
30
40
50
60
70


MgO wt%
MnO wt%
0.0
0.3
0.5
0.8
1.0
1.3
20
30
40
50
60
70



Na2O wt%
1.0
0.8
0.5
0.3
0.0
20
30
40
50
60
70
MnO wt%



P2O5 wt%
0.6
0.4
0.2
0.0
20
30
40
50
60
70
MnO wt%

Chemically the Saidgi Mn-deposits can be termed as Mn-oxide deposits while that of Shuidar can be named as Mn-Fe-oxide deposits because of having Fe_2O_3 upto 15.53 wt% Geochemical criteria to identify ferromanganese deposits of a hydrothermal and hydrogenous origin are well established. Major element ratios and the trace element concentration have been employed to characterize ancient analogues of the exhalative deposits forming at modern active ridges (Crerar et. al., 1982). Iron and Mn are characteristically fractionated on precipitation from hydrothermal solution, producing high or low Fe\Mn ratio in exhalative sediments. In general the relationship 0.1> Fe/Mn > 10 is seen to hold, whereas in hydrogenous deposits the ratio is close to unity (Rona, 1978).

Both Saidgi and Shuidar Mn-deposits are characterized by low Fe/Mn ratio (0.001 to 0.382) and are similar to those found near present day submarine hydrothermal centers where they are formed by rapid precipitation from hydrothermal solution. The Mn-oxide deposits of Saidgai and the Mn-Fe oxide deposits of Shuidar area are having on average Fe/Mn ratio of 0.008 and 0.155 respectively (Table 2). The Fe/Mn ratio is found to be higher in the earlier precipitates (Bonatti et al., 1972). Majority of the data of Manganese ores of both Saidgi and Shuidar areas generally fall within or close to the field defined for hydrothermal deposits (i.e. those formed on the present ocean floor by hydrothermal activity) by Bonatti et. al., (1972) and Crerar et. al., 1982) in figure 5. From this diagram it is clear that the Fe/Mn ratio for hydrogenous Mn-deposits (i.e. the deposits formed by normal sea water) is close to one and is higher for the early precipitates (Bonatti et. al., 1972). Si-Al discrimination diagram (Fig. 6) has been proposed by Peter (1988) for distinguishing the hydrothermal Mn-oxide deposits from that of hydrogenous. Almost all the samples of Saidgi and Shuidar ore bodies fall within the field of hydrothermal deposits in Si-Al diagram (Fig. 6).

Iron in the Saidgi deposits is extremely low as compared to that of Shuidar, suggesting that a complete fractionation of the two elements occurred before the deposition of former. Alumina in these ore bodies could be added primarily from the detrital grains of clay minerals in the sediments (see Crerar et. al., 1982). According to Sugisaki (1984), Ti is generally immobile in hydrothermal solutions and could be a measure of clastic input. The Mn ore bodies of both Saidgi

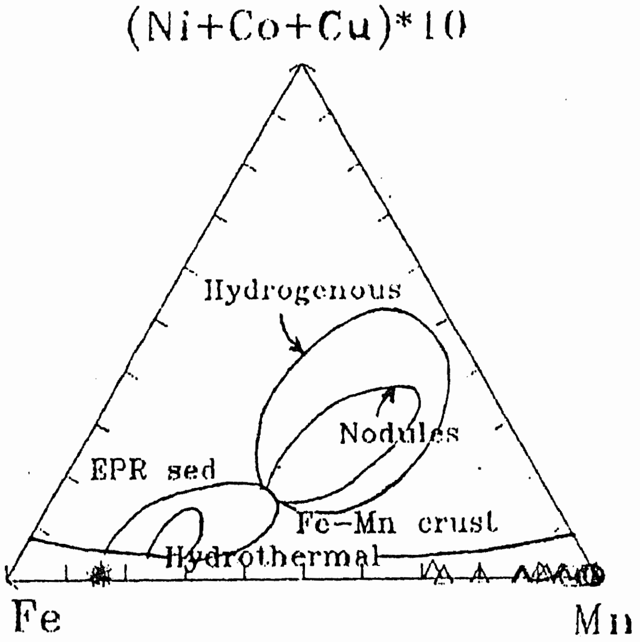


Fig. 5. Mn-Fe-(Ni+Co+Cu)x10 discrimination diagram for the Mn-deposits of Saidgi and Shuidar areas. Various fields are after Bonatti et al. (1972) and Crerar et al. (1982). (Symbols as for fig. 4)

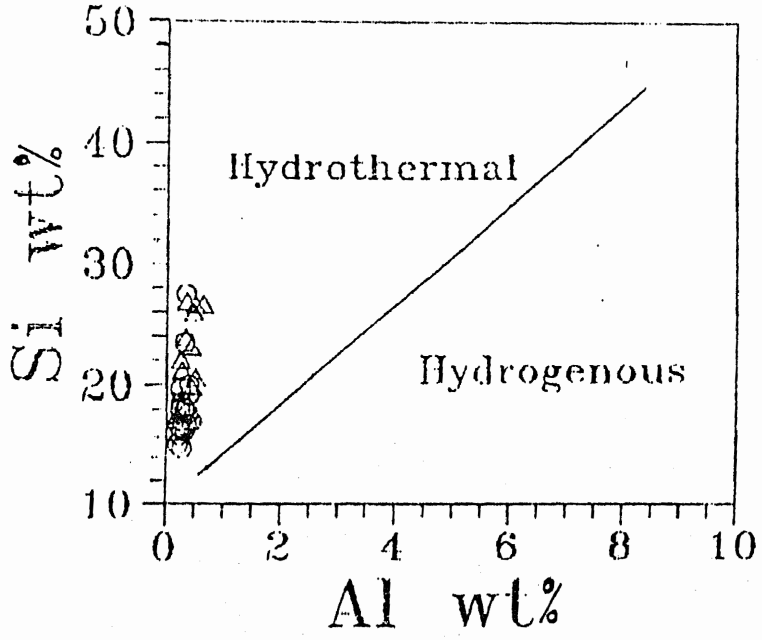


Fig. 6. Si-Al discrimination diagram for the Mn-deposits of Saidgi and Shuidar areas. The solid line separates hydrothermal and hydrogenous deposits (Peters, 1988). (Symbols as for fig. 4)

and Shuidar have relatively high TiO_2 which can be attributed to the mixing of detrital material during precipitation. The contribution of detrital material is further confirmed by an extremely good correlation of TiO_2 and AlO_3 (Fig. 7).

Trace elements

The trace elements in the Saidgai deposits have greater variation. Cu is ranging from 22 to 130 ppm, Pb from 26 to 64 ppm, Zn from 14 to 87 ppm, Ni from 0.00 to 47 ppm, Cr from 12 to 89 ppm and Co is very low (0.00 to 12 ppm). The Shuidar deposits, however, have relatively high concentration of Cu (73 to 320 ppm), Pb (34 to 73 ppm), Zn (34 to 150 ppm), Ni (23 to 76 ppm), Cr (41 to 75 ppm) and Co (15 to 38 ppm).

All the trace elements are plotted against MnO in Figure 8. Ni, Cu, and Co have weakly defined negative correlation against MnO while Zn, Pb and Cr have grater scatter against MnO (Fig. 8). The trace elements (Cu, Pb, Zn, Ni, Cr, Co) are very low in the Mn ore bodies of both Saidgai and Shuidar areas and, therefore, akin to submarine hydrothermal deposits (Bonatti et al., 1972; Crerar et al., 1982, Nicholson, 1992 and Choi and Hariya, 1992). The Shuidar area has high trace element profile as compared to that of the Saidgai area (Fig. 9). The submarine hydrothermal Mn-oxide deposits in most cases (e.g. Mn-oxide deposits of East Pacific Rise and the Galapagos areas) have higher trace elements (Cu, Zn, Ni & Co) as compared to that of pelagic sediments but these are much lower than that of the hydrogenous Mn-Fe deposits (Cronan, 1980). Choi and Hariya (1992) have distinguished the hydrogeneous deposits (i.e. deep-sea Mn-nodules) and submarine hydrothermal Mn-deposits by considering the relationship of Zn, Ni & Co in a ternary diagram (Fig. 10). By plotting the samples of Mn ore bodies of Saidgi and Shuidar areas in this diagram majority of samples plot near the Ni-Zn join where the submarine hydrothermal Mn-deposits are usually plotted. The hydrgenous Mn deposits, having relatively high Co contents, however, occupy the field closer to Co apex in this diagram.

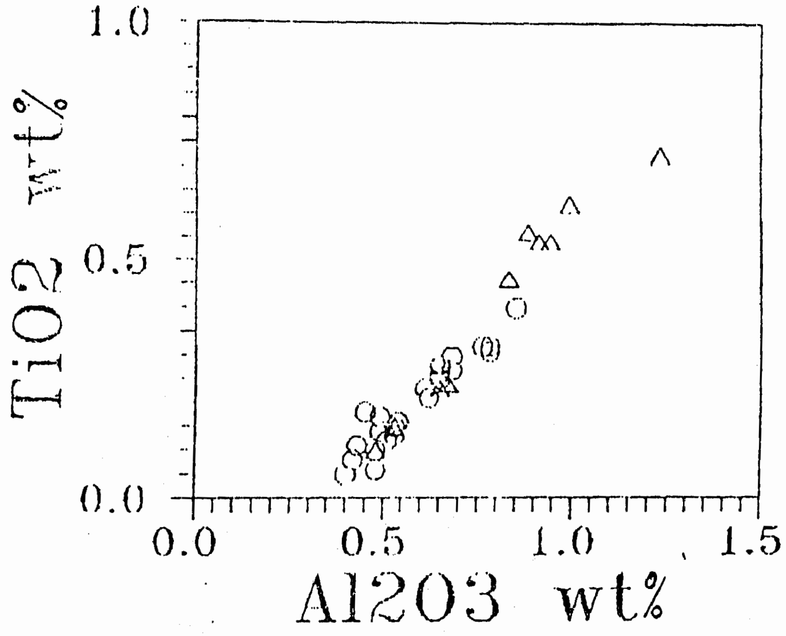


Fig. 7. TiO_2 Vs Al_2O_3 diagram for the Mn-deposits of Saidgi and Shuidar areas. (Symbols as for fig. 4)

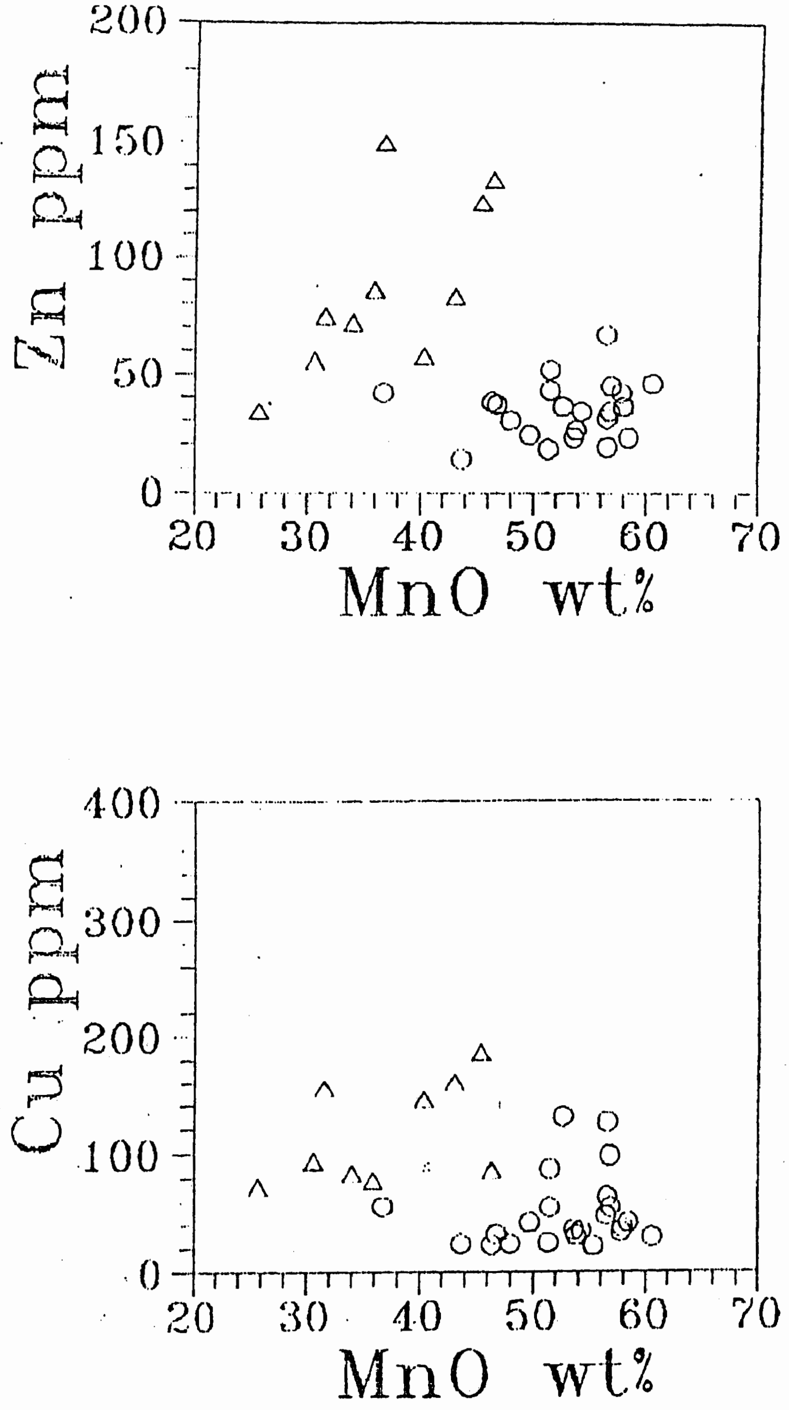
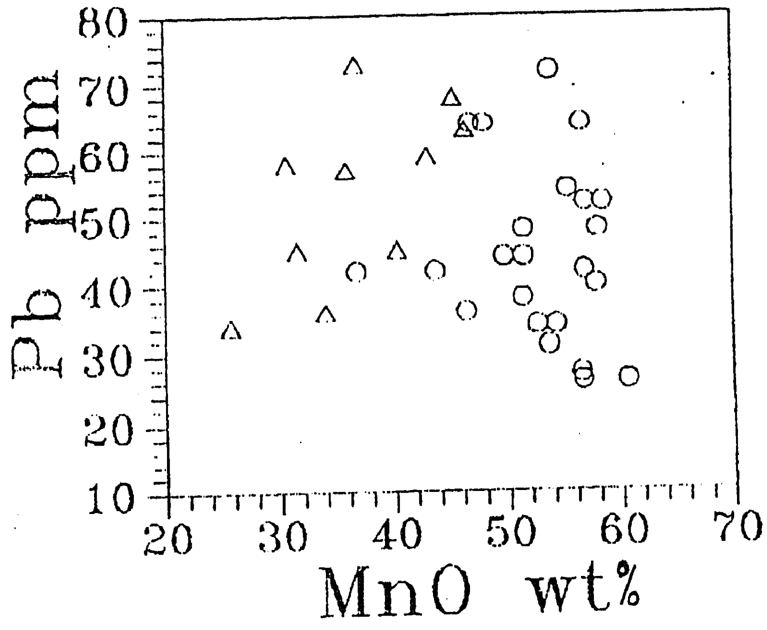
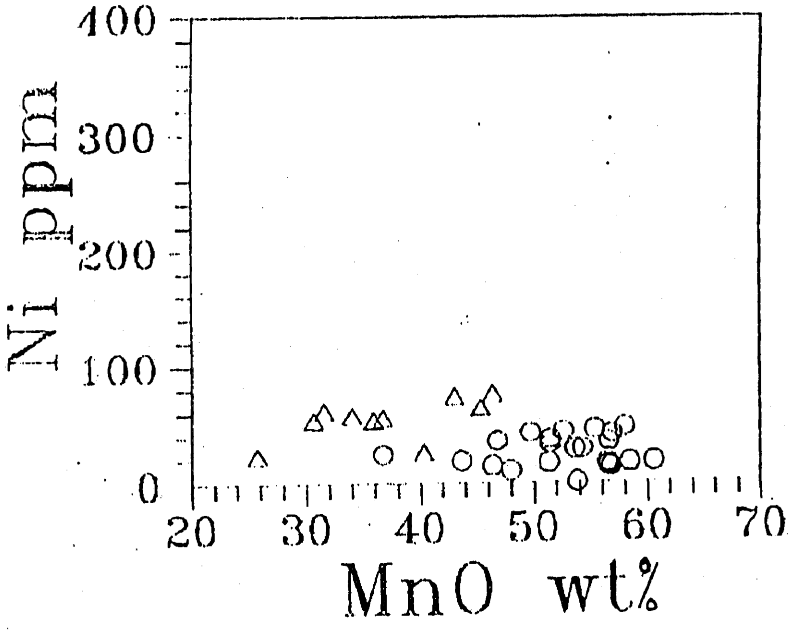


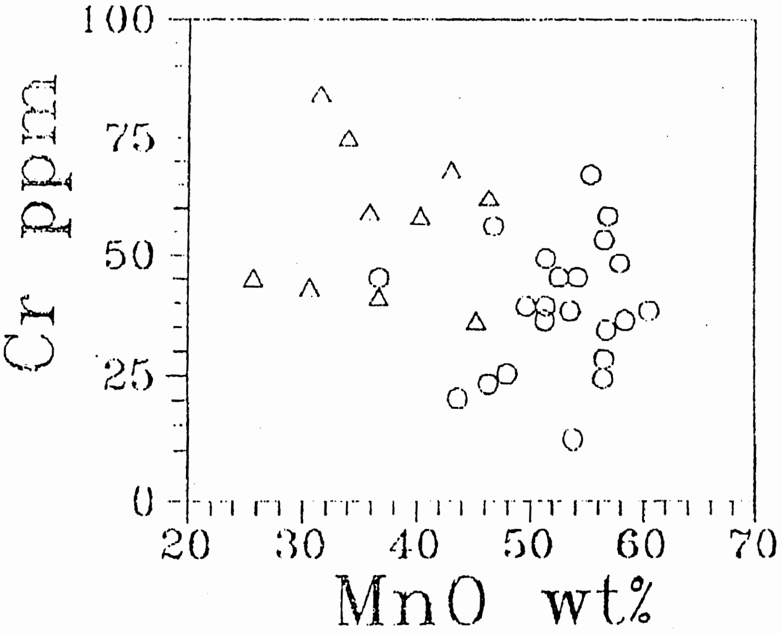
Fig. 8. Plot of Cu, Zn, Ni, Pb, Cr, Co Vs MnO fro the Mn-deposits of Saidgi and Shuidar areas. (Symbols as for fig. 4)



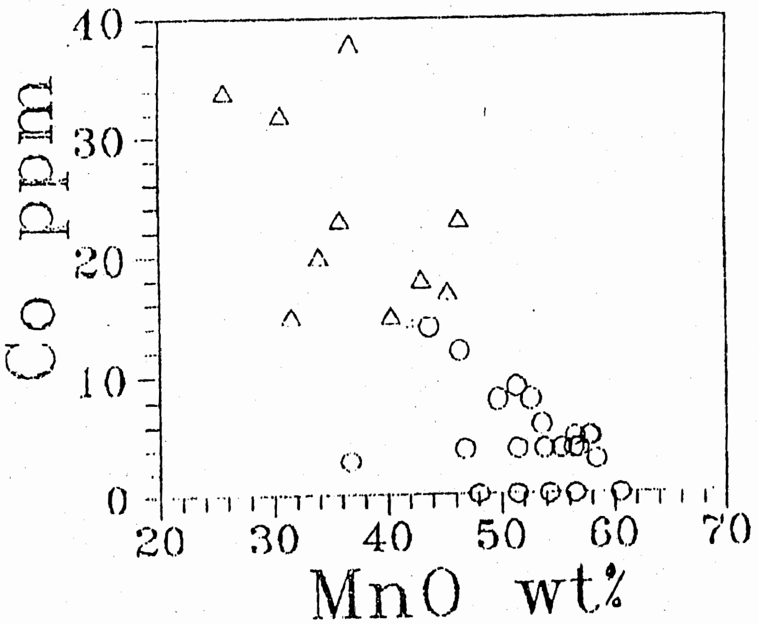
Pb ppm
80
70
60
50
40
30
20
10
20
30
40
50
60
70
MnO wt%



Ni ppm
400
300
200
100
0
20
30
40
50
60
70
MnO wt%



100
75
50
25
0
Cr ppm
20
30
40
50
60
70
MnO wt%



40
30
20
10
0
Co ppm
20
30
40
50
60
70
MnO wt%

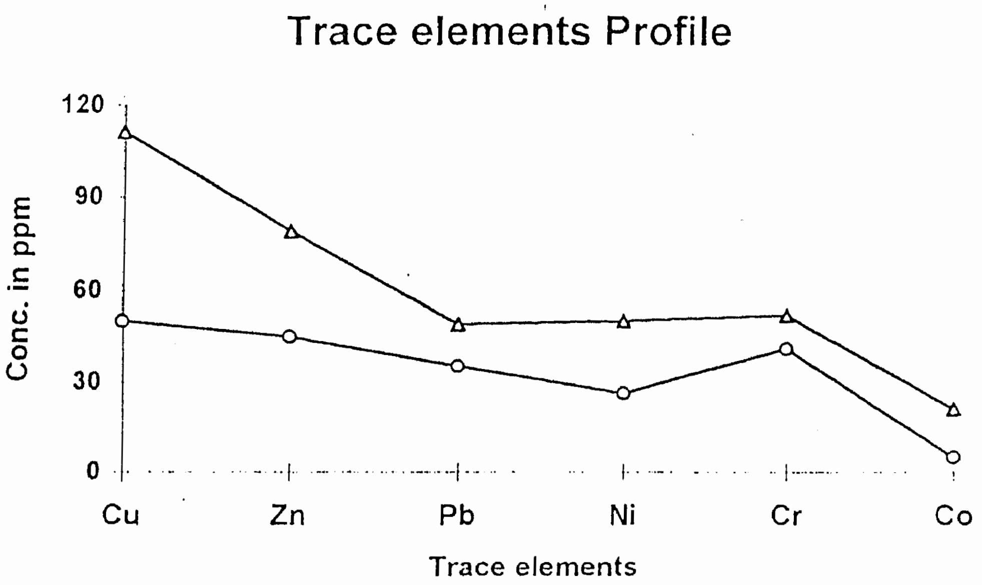


Fig. 9. Representative trace element profiles for Mn-deposits from Saidgi and Shuidar area.

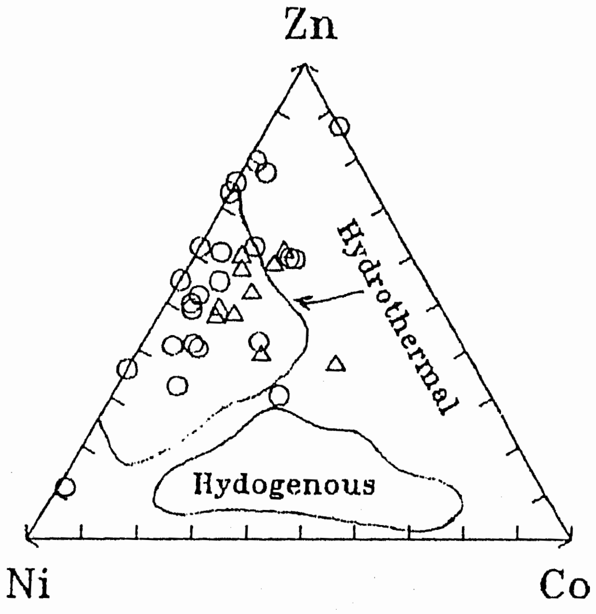


Fig. 10. Zn-Co-Ni diagram for Saidgi and Shuidar Mn-deposits, showing fields of hydrothermal and hydrogenous deposits (Choi and Hariya, 1992). (Symbols as for fig. 4)

Table3. Comparison of average chemical composition (wt%) of Saidgi and Shuidar Mn-deposits with the Mn-deposits of different modern geological settings.

	1	2	3	4	5
Mn	40.83	26.01	39.04	34	22
Fe	0.34	4.02	0.046	3.83	15
Mn/Fe	120	6.47	847	8.87	1.46
Co	0.001	0.002	0.002	0.008	0.630
Ni	0.004	0.005	0.035	0.043	0.440
Cu	0.005	0.011	0.0043	0.022	0.800
Mn/Co+Ni+Cu	4083	11445	947	465	10.43

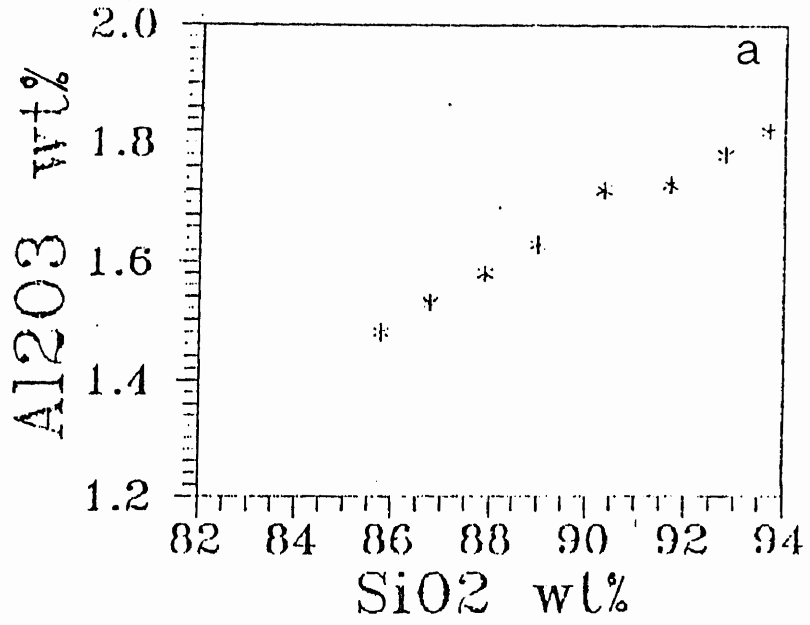
1&2 = average Saidgi and Shuidar respectively (this study);
3 = TAG field, mid-Atlantic ridges (Scott et al., 1976;
4 = Bonin arc, north west Pacific (Usui et al., 1981);
5 = average hydrogenous Pacific crust (Hein et al., 1988).

Table 4. Summery of the characteristics of studied Mn-deposits compared with the Apenine ophiolite, metallifrous sedimentary deposits, hydrothermal and hydrogenous metalliferous deposits from the modern oceans (after Bonatti et al., 1976).

Mn-deposits of this study	Apenine ophiolite metalliferous sedimentary deposits	Hydrothermal submarine metalliferous sedimentary deposits	Hydrogenous submarine metalliferous sedimentary deposits
Associated with chert just above the volcanic unit (basalt and basaltic-andesite)	Associated with chert just above the basalt unit	Associated with chert just above the basalt basement	no any specific relationship
Fe/Mn ratio extremely low (<0.15)	Fe/Mn ratio extremely low (<0.1)	Fe/Mn ratio ranging from extremely low (<0.1) to extremely high (>10)	Fe/Mn ratio ranging between >0.5 & <5
Concentration of trace elements (Ni, Co, Cu, Zn) is low relative to Fe+Mn	Concentration of trace elements (Ni, Co, Cu, Zn) is low relative to Fe+Mn	Concentration of trace elements (Ni, Co, Cu, Zn) is generaly low relative Fe + Mn	Concentration of trace elements (Ni, Co, Cu, Zn) is generaly high relative Fe + Mn

Table5. Chemical composition of metachert of Saidgi and Shuidar areas, north Waziristan.

S.No.	WSC22	WSC32	WSC17	WSC20	BTC14	BTC10	BTC15	BTC21	average
SiO2	88.98	92.78	87.89	90.34	86.78	91.67	85.78	93.67	89.74
TiO2	0.06	0.04	0.08	0.08	0.1	0.05	0.1	0.03	0.07
Al2O3	1.63	1.78	1.58	1.72	1.53	1.73	1.48	1.82	1.66
Fe2O3	3.15	2.65	3.21	2.98	3.35	2.84	3.47	2.52	3.02
MnO	0.54	0.42	0.56	0.45	0.58	0.46	0.59	0.41	0.50
MgO	1.23	0.87	1.34	1.1	1.45	0.98	1.78	0.62	1.17
CaO	1.25	0.34	1.65	1.34	1.45	0.67	1.89	0.47	1.13
Na2O	0.67	0.42	0.56	0.56	0.68	0.48	1.23	0.06	0.58
K2O	0.48	0.24	0.78	0.49	0.74	0.39	0.89	0.04	0.51
P2O5	0.34	0.23	0.34	0.26	0.34	0.23	0.44	0.24	0.30
L.I.O	0.78	0.54	0.76	0.63	0.78	0.63	0.82	0.34	0.66
Total	99.11	100.31	98.75	99.95	97.78	100.13	98.47	100.22	99.34
Cu	12	10	4	8	15	9	18	21	12
Pb	4	5	7	2	0	0	3	4	3
Zn	5	0	3	6	4	2	7	3	4
Ni	0	2	4	0	2	3	2	0	2
Cr	2	2	3	0	3	5	6	3	3
Co	2	0	0	0	1	3	2	0	1
Fe/Mn	5.268	5.698	5.177	5.981	5.216	5.576	5.312	5.551	5.444



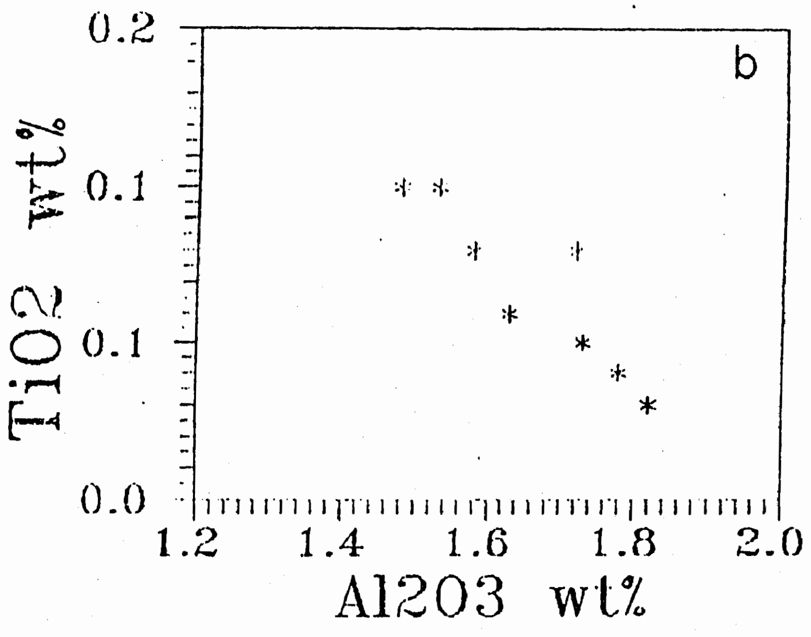
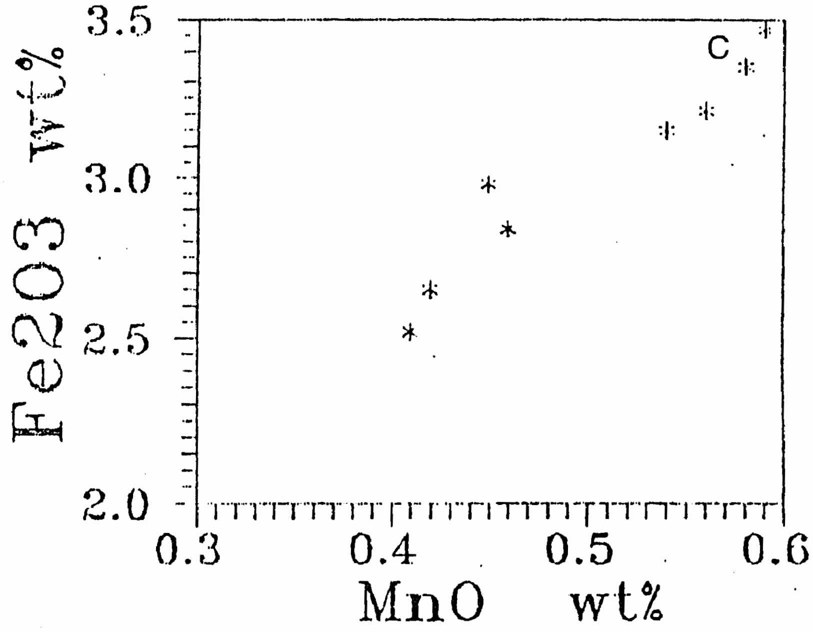
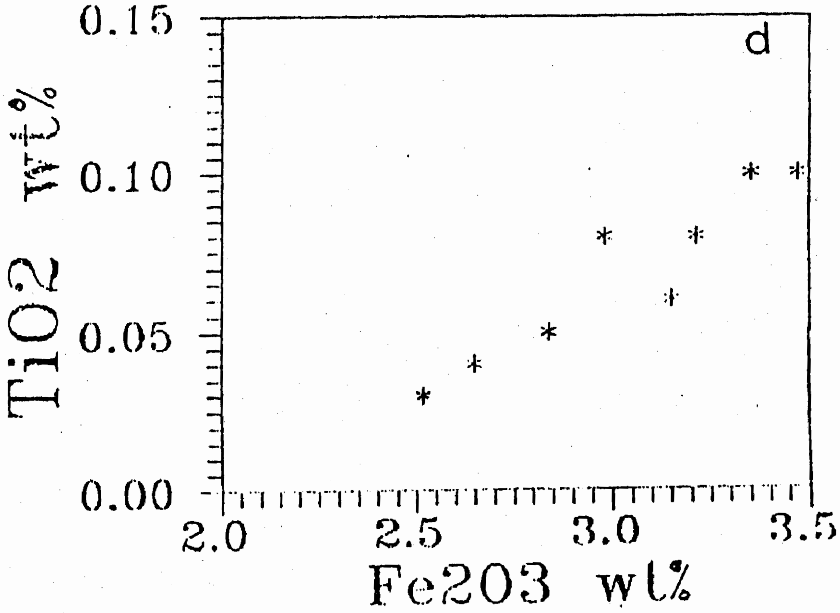
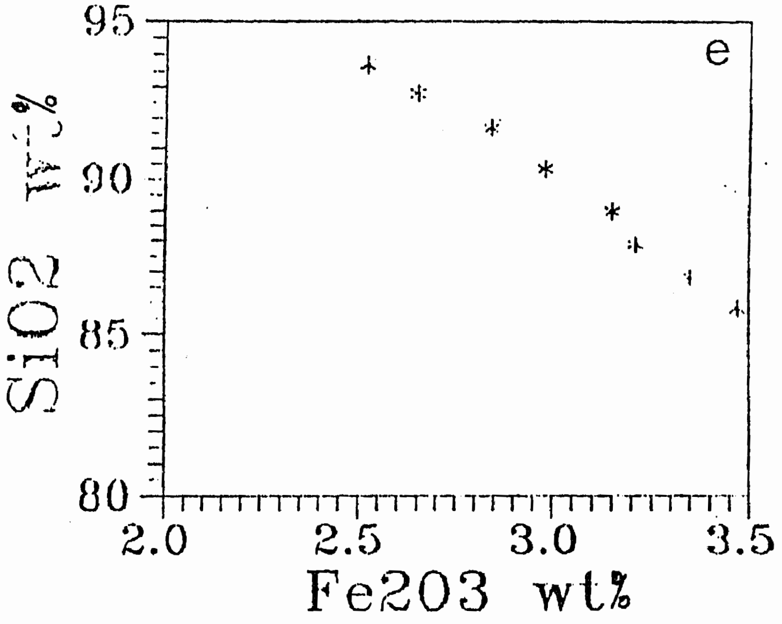
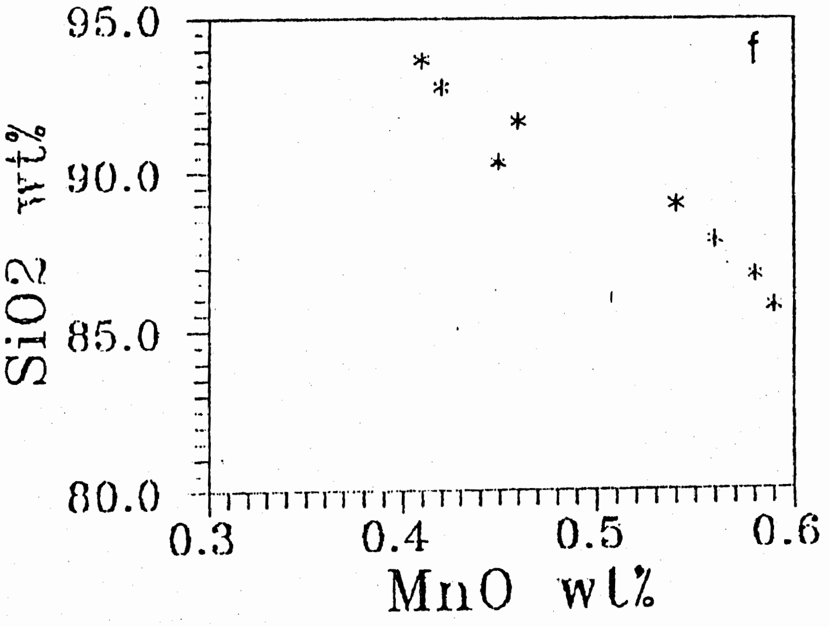


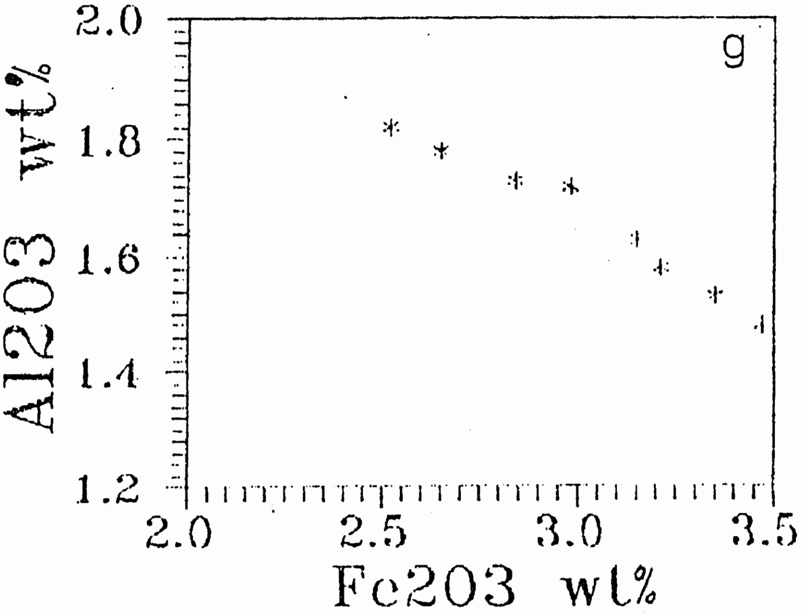
Fig. 11. Plots of (a)Al_2O_3 Vs SiO_2, (b)TiO_2 vs Al_2O_3, (c) Fe_2O_3 vs MnO, (d) TiO_2 vs Fe_2O_3, (e) SiO_2 vs Fe_2O_3, (f) SiO_2 vs MnO, (g) Al_2O_3 vs Fe_2O_3, and (h) Al_2O_3 vs MnO for the Mn-deposits of Saidgi and Shuidar areas.

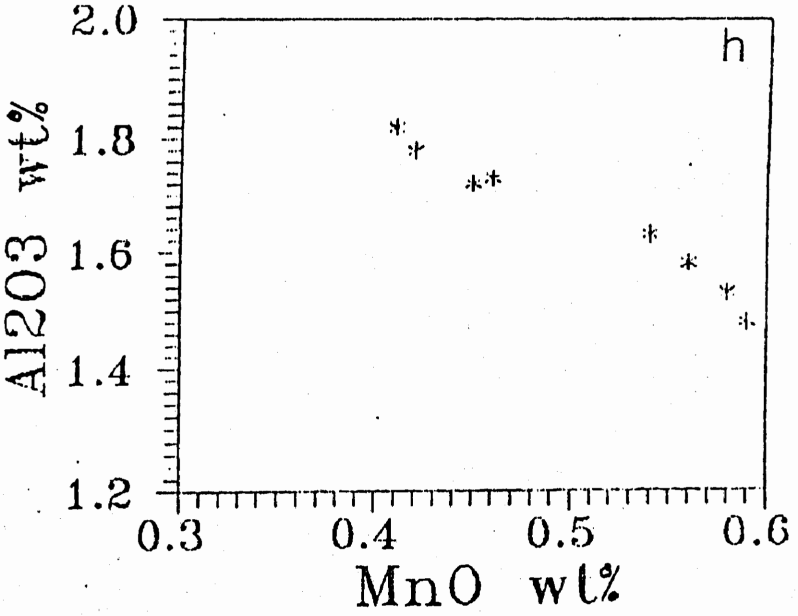

c
Fe2O3 wt%
MnO wt%
3.5
3.0
2.5
2.0
0.3
0.4
0.5
0.6


d
TiO2 wt%
Fe2O3 wt%
0.15
0.10
0.05
0.00
2.0
2.5
3.0
3.5


e
95
90
85
80
SiO2 wt%
2.0
2.5
3.0
3.5
Fe2O3 wt%


f
95.0
90.0
85.0
80.0
SiO2 wt%
0.3
0.4
0.5
0.6
MnO wt%


g
Al2O3 wt%
2.0
1.8
1.6
1.4
1.2
2.0
2.5
3.0
3.5
Fe2O3 wt%


h
Al2O3 wt%
2.0
1.8
1.6
1.4
1.2
0.3
0.4
0.5
0.6
MnO wt%

The studied Mn-deposits are associated with the pillow lavas. The trace element chemistry of these pillow lavas is not known yet but it is suggested that these pillow lavas may have been erupted in an environment similar to that of present day ocean ridges and that the hydrothermal component contained in the ore bodies was derived from the hydrothermal emanations along active spreading centers.

The average major and trace element data of the studied Mn & Mn-Fe deposits of Saidgi and Shuidar areas respectively have been compared with that of the other geogical settings in Table 3. The studied deposits have geochemical similarities, especially Mn/Fe & Mn/Co+Ni+Cu ratio, mainly with that of the spreading centers and in some respect with that of island arc. It is evident from Table 4 that the studied Mn-deposits have many characteristics similar to that of the Apennine ophiolite metalliferous deposits (Bonatti et al., 1976). This suggest that these deposits are not similar to modern hydrogenous deposits but are equivalent to those formed on the modern ocean floor by the hydrothermal activity mainly along spreading centers.

METACHERTS

The metachert has SiO_2 in the range of 85.78- 92.78 wt%, Al_2O_3 (1.48- 1.82 wt%), TiO_2 (0.03- 0.1wt%), Fe_2O_3 (2.52- 3.35 wt%), MnO (0.41-0.59 wt%), MgO (0.62-1.78wt%), CaO(0.47-1.89wt%), Na_2O(0.06-1.23 wt%), K_2O(0.04-0.89wt%), and P_2O_5(0.23-0.44wt%) (Table 5). Among the trace elements Cu is ranging from 4 to 21 ppm, Pb from 0 to 7 ppm, Zn from 0 to 7 ppm, NI from 0-4 ppm, Cr from 0 to 6 ppm and Co from 0-3 ppm (Table 5).

Among the major element oxides Al_2O_3 vs SiO_2 (Fig.11a) Al_2O_3 Vs TiO_2 (Fig-11b), Fe_2O_3 vs MnO (Fig-11c), Fe_2O_3 vs TiO_2 (Fig-11d) show positive correlation. However, SiO_2 and Al_2O3 show negative correlation against Fe_2O_3 and MnO (Figs. 11e,f & 11g,h respectively). This is a reflection of the increase in iron and Mn oxides at the expense of quartz and clays component. The close association and interbeded nature of metachert with the Mn deposits in Saidgi and

Shuidar areas suggest that both could be syngenetic and might have originated by the similar processes. This could be ascertain by considering the geochemistry of these metacherts.

Several geochemical discrimination diagrams have been established, on the basis of major and trace elements, to assist in metallogenic interpretation (See Bonatti et al., 1972 Crerare et. al., 1982; Adachi et al., 1986; Meylan et al., 1981; Nicolson, 1992). These authors have demonstrated that the hydrothermal sediments (especially cherts) can be identified on the basis of their Si, Fe, Mn, Al, Ti, Co, Cu, and Ni contents (Figs. 12 to 16). The metachert samples of both Saidgi and Shuidar areas are plotted in these discrimination diagrams. These samples consistently plot within the hydrothermal field in these diagrams (Figs. 12 to 16).

The metacherts of both Saidgi and Shuidar ore bodies have Fe/Mn ratio in the range of 5.18 to 5.70 with an average value of 5.44 (Table 5). This value is typical of hydrothermal origin. Usually Silica in the form of ferrugineous silica gel in the hydrothermal Mn-deposits is formed by submarine effusive processes (Bamba, 1984). The conformable nature of the studied Mn-deposits and the associated metachert suggests that the Mn and Si were probably precipitated together during their formation. The metacherts are having rounded or oval shape radiolarian, present within the microcrystalline quartz and chalcedony matrix. This suggest that the metachert of the area are formed from the hydrothermal silica as well as from biogenic silica. It is also clear from the chemistry of the studied metachert that these are formed at least by the similar processes as the Mn-deposits and that could be the exhalation of hydrothermal fluid along the spreading centers.

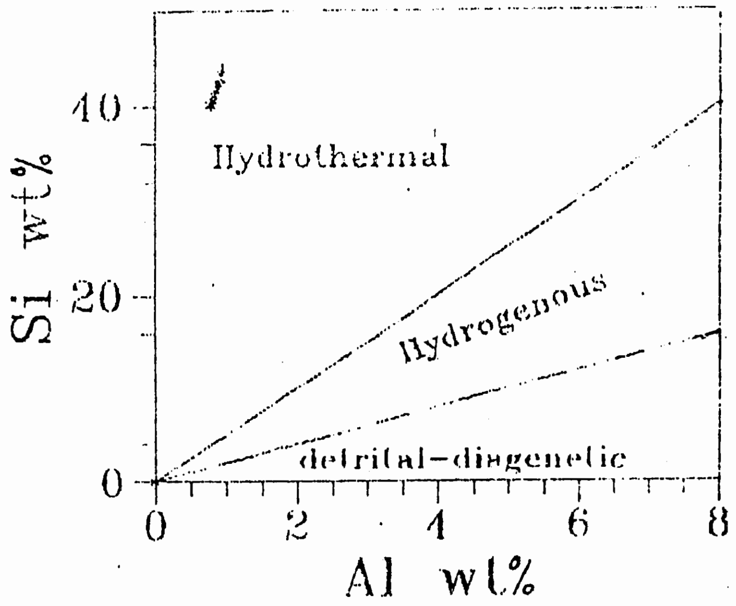


Fig. 12. Si vs Al discrimination diagram for the metachert of Saidgi and Shuidar areas. Various fields are after (Crerar et al., 1982).

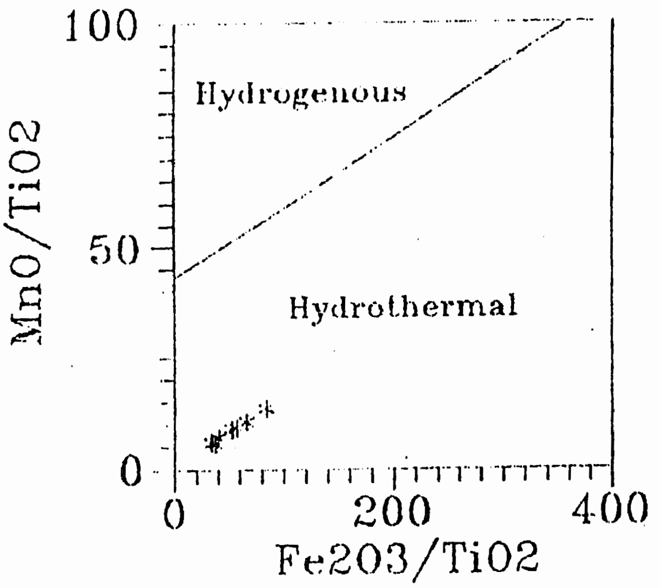


Fig. 13. MnO/TiO_2 vs Fe_2O_3/TiO_2 diagram for the metacherts of Saidgi and Shuidar areas. Solid lines separates the cherts of hydrothermal and hydrogenous origin (after Adachi et al., 1986).

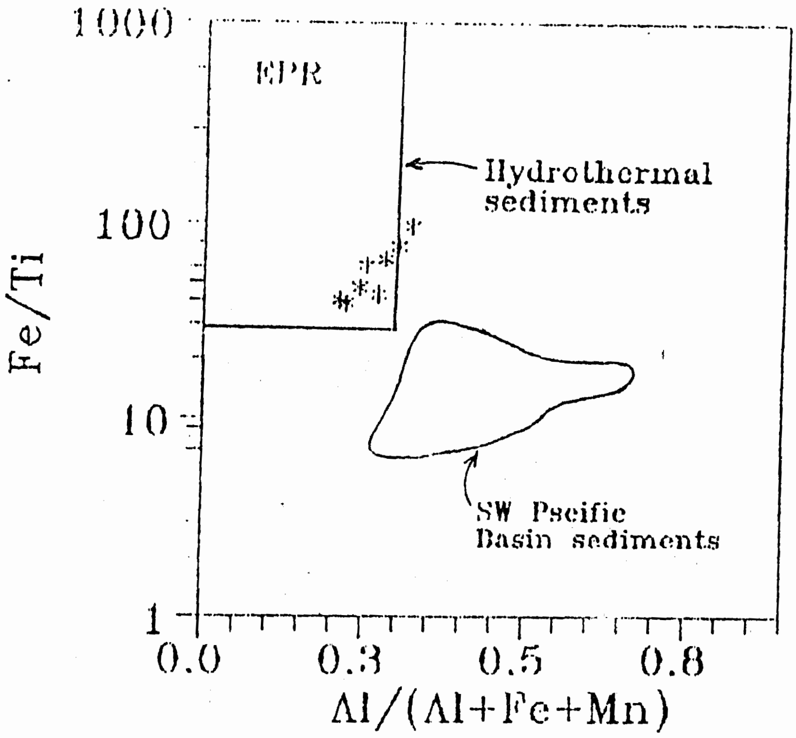


Fig. 14. Plot of metal ratios for marine sediments of hydrothermal and terrigenous origin (after Nicholson, 1992). Metachert of both Saidgi and Shuidar areas fall within the field of hydrothermal sediments.

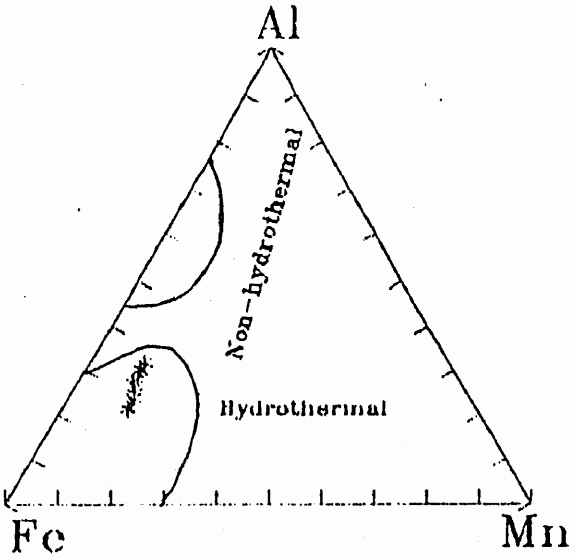


Fig. 15. Al-Fe-Mn diagram for the metacherts of Saidgi and Shuidar areas. Various fields are after Adachi et al. (1986).

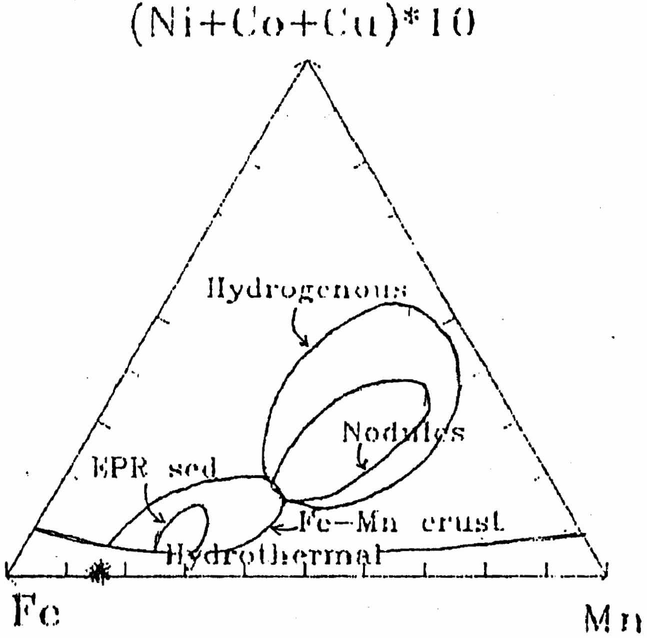


Fig. 16. Fe-Mn-(Ni+Co+Cu)x10 discrimination diagram for the metachert from Saidgi and Shuidar areas. Various fields are after Bonatti et al. (1972) and Crerar et al. (1982).

CHAPTER - 7

CONTROLLING FACTORS FOR THE FORMATION OF WAZIRISTAN MANGANESE DEPOSITS

It has already been established by the major and trace element geochemistry of the Mn-deposits of Waziristan area (both Saidgi and Shuidar areas) that these deposits are similar to those of the present day submarine hydrothermal deposits originated at the spreading centers.

The submarine hydrothermal solutions are produced due to the hydrothermal circulation of sea-water through fractionated oceanic crust (up to several kilometer at depth) along spreading centers. This downward flow of the sea-water leads to progressive warming and reduction (through volcanogenic heat sources) and an increase in acidity which ultimately result in increase in temperature of sea-water and, therefore, form hydrothermal solution of low intensity ($\leq$200 ^{0}C) and high-intensity (>200 ^{0}C to 400 ^{0}C) (Roy, 1992). These hydrothermal solutions are capable of extracting metals from the volcanic rocks during their subbottom circulation, (Bonatti, 1976, Rona, 1984). Bostrom (1974) suggested the volatile, derived directly from the degassing of the upper mantle, to be an additional source of elements to the circulating sea-water. The metal enriched hydrothermal solution is convicted upward through the oceanic crust and upon discharge on the sea-floor it starts precipitating different metals/elements as sulfides and oxides-hydroxides. This deposition is totally dependent on the decrease in temperature and pressure and increase in Eh and/or pH of the hydrothermal solution (Roy, 1992). These studies, although, are based on the research carried out on the modern ocean basins, however, these can be correlated with the generation of metalliferous fluid in ancient oceanic basin along ocean spreading centers.

Ophiolite complexes have been recognized as representing uplifted (obducted) fragments of old oceanic crust and upper mantle. Therefore, the ophiolitic metalliferous deposits are considered to be the analogue of the metalliferous deposits produced along active oceanic ridges in the present day-oceans. The formation of the Mn-deposits of Saidgi and the Mn-Fe deposits of Shuidar could be related to the same phenomenon within the Neo-Tethys ocean where these deposits have been originated along sea-floor- spreading centers and are later on obducted on land (i.e. existing position) along with other ophiolitic rocks of the area. Subsequent metamorphism during and after emplacement (obduction) of the ophiolitic bodies caused some recrystallization and small-scale elemental remobilization but left intact the essential geochemical characteristics of the deposits (see also Bonatti, 1976). By considering the models of Bonatti et al. (1976); Canon and Force (1983) and Buhan (1992) a very simplified hypothetical model has been proposed for the Mn-deposits of both Saidgi and Shuidar areas in Figure 17. Similar type of ophiolite complexes hosting Mn-deposits have also been reported elsewhere in the world (Bonatti et al., 1976; Fleet and Robertson, 1980; Lee, 1982; Crerar et al., 1982; Robertson and Boyle, 1983; Chyi et al., 1984; Roy, 1992).

Both Mn-deposits of Saidgi and Mn-Fe deposits of Shuidar in Waziristan are spatially separated from each other. The Mn-deposits of Saidgi occurring in the north is relatively bigger than the Mn-Fe deposits of Shuidar which is located about 15 Km south east (Fig.1). Both these deposits though occur at a distance but might have related genetically. The addition of Fe in the Shuidar Mn-Fe deposits could be related to the Physio-chemical change after the exhalation of the hydrothermal solution on the sea floor.

Substantial amount of Mn along with Fe is introduced into sea water by the hydrothermal solution along sea-floor spreading centers. As the Fe compounds are less stable in the hydrothermal solution, therefore, they tend to precipitate first, close to the source, while the Mn compounds are relatively stable and maintain longer residence time in solution. Mn deposition, therefore, takes place distal to the hydrothermal vent (Panagos and Varnavas, 1984, Roy 1992). The Eh and/or pH of hydrothermal solution also has great control on the precipitation of Mn and Fe and their compounds (Kranskopf, 1957; Hem, 1972; Frakes and Bolton, 1992; Roy, 1992). Mn is most mobile relative to Fe during low Eh and/or pH conditions. Therefore, in response to a gradual increase in Eh and/or pH, more precipitation of Fe hydroxides will take place before Mn oxides begin to precipitate. This fractionation of Mn compounds from Fe compounds suggest-spatial variation in Eh and/or pH dependent upon the site of deposition of these two types (Roy,

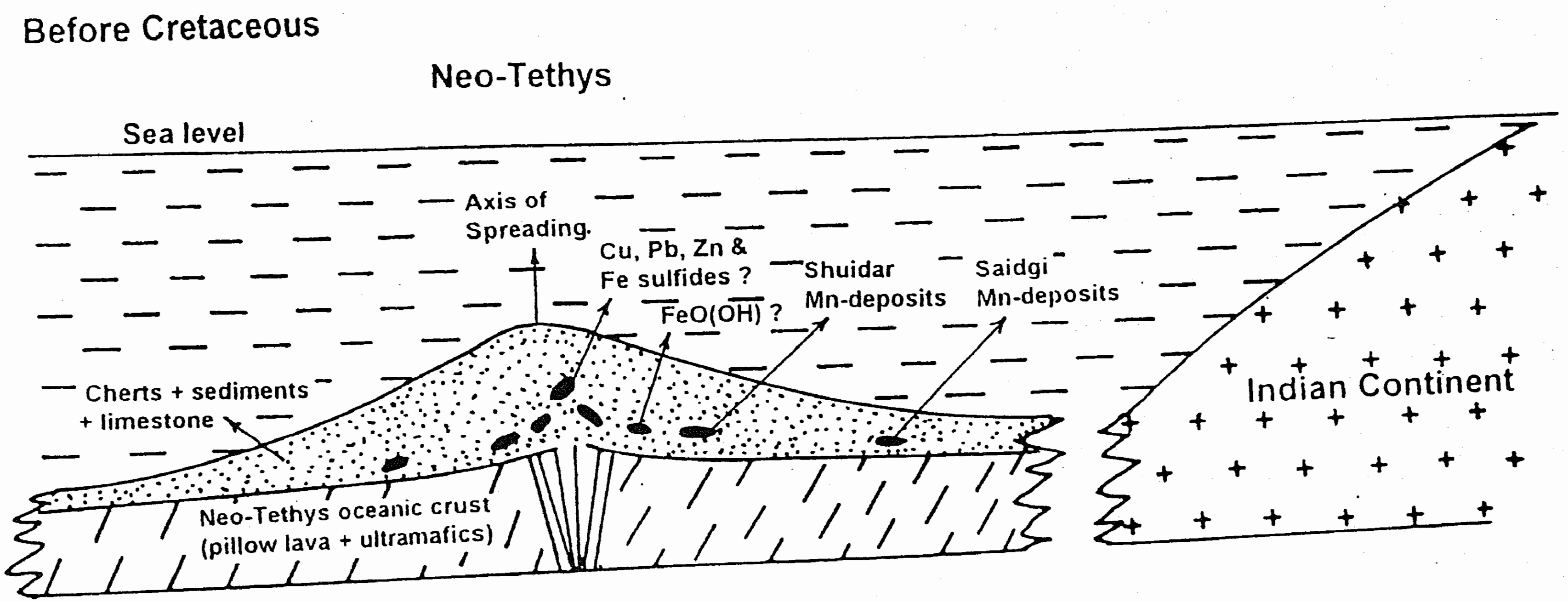


Fig. 17. Hypothetical diagram showing the geological environment for the formation of Saidgi and Shuidar Mn-deposits of the Waziristan ophiolite complex.

1992). The separation of Mn deposits of Saidgi and Mn-Fe deposits of Shuidar can also be attributed to the same phenomenon.

The relative higher concentration of trace elements in Mn-Fe deposits of Shuidar than that of Mn-deposits of Saidgi may also suggest that the trace elements might have behaved in the same manner as the Fe did during precipitation of these two types of deposits. These trace elements along with Fe might have spatially removed (or precipitated) earlier owing to the greater solubility of manganese (Roy, 1992).

From this whole discussion it can be concluded that the Mn-deposists of Saidgi and the Mn-Fe oxide deposits of Shuidar are cogenetic and are formed by the submarine hydrothermal solution in an ocean-floor spreading environment. This hydrothermal solution was enriched in divalent Mn and to some extent divalent Fe ions. The source must have been nearer to the Shuidar deposits, where the Fe oxides along with Mn oxides have been precipitated near the source and then there was successive precipitation of Mn-oxide in the form of Saidgi Mn-deposits. This whole phenomenon might have occurred due to an increase in the Eh and/or pH of the solution away from the source. As already mentioned that both these deposits are a part of the Waziristant ophiolitic sequence, the occurrence of these deposits at the present situation could not be analogue of the past. Therefore, it is not possible to ascertain the exact location of the source vent and also the movement direction of the hydrothermal solution. However, it could be worth mentioning that the study area has both near vent (i.e. Shuidar Fe-Mn deposits) and distal vent (Saidgi Mn-oxide deposits) Mn-deposits.

Buhn et al. (1992) has suggested a model for the provenance of the ore-forming solutions derived from hydrothermal vents in modern oceanic basins. In this model they have presented systematic formation of base metal (Cu, Fe, Zn etc.) sulfide near the vent and then systematic precipitation of Fe-Mn and Mn deposits depending on the activity of sulfur, change in temperature, and other parameters such as Eh and pH. Therefore, the base metals are of low concentration in the Mn-deposits formed by hydrothermal process (Bonatti, 1975). If this model can be applied to the studied deposits, then the possibility of presence of exhalative base metal sulfides near to the Shuidar Fe-Mn deposits can not be ruled out. Copper sulfide mineralization has, however, been reported at Shinkai (Boya) area ~ 20 km north-east and ~10 km south of Shuidar and Saidgi area respectively (Badshah, 1983 &1985). The exploration work is still in progress by the FATA. DC in this area. According to this model there could be the possibility that this copper mineralization in Shinkai area could be related to the similar phenomenon and may be of exhalative type as also suggested by Mian & Afridi, (1994) and Wang, 1996). Further investigations are, therefore, mandatory in this regard. Bonatti (1975) has suggested that the non-existence of sulfide deposits in association with the Mn-deposits can be attributed to the rapid rate of accumulation of hydrothermal deposits which limits the opportunity of "scavenging" of minor metals from sea water by Fe and Mn hydroxide. If there are no stratiform sulfide deposits in the study area then low concentration of trace elements in the studied manganese deposits could be related to the similar phenomenon as suggested by Bonatti (1975).

CHAPTER - 8

ECONOMIC GEOLOGY

As already mentioned that the manganese deposits are mainly present in Saidgi and Shuidar areas of north Waziristan agency. However, manganese showings are also noticed in Tut Narai and Mahamad khail areas, which have less economic importance. The manganese deposits of Saidgi and Shuidar areas have greater economic importance. These deposits are, therefore, evaluated from economic point of view.

A. MANGANESE DEPOSITS OF SAIDGI AREA

The manganese deposits of Saidgi area are hosted by metachert / jasperite following the general trend of host rocks (i.e. striking N40E and dipping 40-45NW (Fig. 2a). The exposed length of the ore body is about 62 meter with variable thickness. The thickness decrease from south to north having an average thickness of 6 meters. The thickness of the body also increases from top to bottom. A separate 15 cm bed of manganese lies in the western side which runs parallel to the main body having a length of about 60 meters. Chemical analyses show that the deposit is of better grade having 36 - 60 wt% MnO content with an average content of 52 wt% (Table 2).

A total inferred reserves of about 34000 metric tons for manganese ore deposits in Saidgi area has been calculated as follows:

a) **Main Body.**

Exposed length. = 62 meters.
Average thickness. = 06 meters.
Exposed depth above the surface level = 12.12 meters.
Mineable depth below the surface level = 15.15 meters
Total depth. = 27.27 meters.
Volume. = 62*6*27=10144.44 cubic meters.
Specific gravity = 3.27
Tonnage. = 33172.32 metric tons.

b) **Western Bed.**

Exposed length. = 60 meters.
Average thickness. = 0.16 meters.
Mineable depth. = 20.00 meters .
Volume. = 192 cubic meters.
Specific gravity . = 3.27
Tonnage. = 627.84 metric tons.

C) **Total Reserves of the Deposit.**

33172.32+627.84 =33800 metric tons.

B. MANGANESE -DEPOSITS OF SHUIDAR AREA

In Shuidar area about 11 manganese ore zones are exposed in the form of veins, layers and lenses at several places in Barzai and Zebai (Fig. 2b) which are concordant to the host rock (metachert / Jasperites). The MnO contents of these ores are low (31-46 wt%) and high Fe_2O_3 (2-16 wt%) as compare to that of Saidgi Mn-ores (Table 2).

In Barzai area the thickness of the beds varies from 8 cm -1/2 m. Among these zones three zones (zones 1,2 &3; Fig. 2b) seam to be more promising. Zone 1 (Fig. 2b) is the most promising zone in Barzai area. It has the maximum thickness of 30 cm and a length exceeds 200 m. Zone 2 (Fig. 2b) is the second important Zone in Barzai area. It has exposed length of about 60 m and a thickness ranging from 2 - 25 cm. Zone 3 (Fig. 2b) has a length of 40 m and a thickness varies from 2 cm to 20 cm . Several small bands separated by a metachert / jasparites constitute the mineralized zone. The other remaining deposits are smaller in size and do not worth mentioning.

In Zebai area, four ore zones are discovered. Among these, three zones (zones 4, 5 and 6; Fig. 2b) are important. These include manganese ores of Shuidar top (zone 4), Jawar top (zone 4) and Amin jan kot (zone 6). In Shuidar top the Zone 4 is exposed and has a thickness of ~1/2 m and a length of about 400 m. It is present within the matachert / jasperite and is concordant to the host rocks. The rocks are extremely folded and faulted. Zone 5 is exposed in Jaur top area where it has a thickness of about 30 cm and a length of 150 m. Here the rocks are also extremely folded and faulted. Zone 6 is exposed in Amin jan Kot area. It is about 1/2 m thick and about 100 m long homogenous zone interbedded with metachert / jasperite. Structurally this zone is also disturbed. No reserve estimates are calculated for Shuidar deposits. However, some of the ore zones seem to be of economic value if properly treated.

Generally , low grade manganiferous iron ores are only used in the manufacturing of spiegeleisin, but for other purposes the ore should contain 35-46 wt% Mn and not more than 6 wt% Fe , 8 wt% $SiO2$ and less than 1.5 wt% phosphorous. In this respect the manganese ore body of Saidgi area can be used for many purposes after treating it with further benificiation processes. This body is easily accessible through an unmetalled road which is being used for lorries and trucks. Therefore, the transportation of raw material can very easily be carried out with relatively low cost. Some of the shuidar ore zones can also be made economical after further processing it for Mn preconcentration and removal of Si and Fe.

LOCAL MARKET DEMAND

Manganese has got a big demand in Pakistan as well as in foreign countries . Steel, paint, battery cells , glass and textile industries are the main consumers of manganese. The consumption of manganese in Pakistan can be judged from the fact that over millions of rupees per month are spent on the import of manganese oxides. Besides extensive consumption in steel industries, about 1200 metric tons of manganese dioxide is imported for use in Battery cells, paints, glass, textiles and poultry feed. The battery grade is imported from Japan and Chemical grade from China and Singapore. The other countries from where Pakistan imports manganese to fulfill its industrial need include Malaysia, Thailand, South Korea and Turkey.

USES OF MANGANESE

1. It is used for the production of speigleiesen, which is a ferro-manganese substitute in the ordinary steel. This alloy of iron containing less than 20 % Mn, low grades of manganeferrous iron ore may be used.

2. It is used in manufacturing of high grade steel. Presently not a single ton of steel is made without manganese added to it in one form or another .

3. Alloys of manganese with non-ferrous metal, such as copper, are of great importance. These alloys are used for corrosion -proof reservoirs, ships screws etc.

4. Manganese- Aluminum alloys are used in air craft industry.

5. It is also used in various chemicals and for that purpose certain varieties of high grade manganese di-oxide are used .

6. There are many other uses of manganese such as in dry batteries, medicine , carbon mono-oxide gas masks , drying oils , lubricants and wax. It is also used by the glass industries (for discoloring green glass) and for pottery pigments.

CHAPTER - 9

BENIFICIATION STUDIES

Benificiation / upgradation of ore is the pre-concentration of target metal within the ore deposits up to the desired level. Various techniques are being used throughout the world for upgradation of many types of ores as per requirement of many industries.

It has already been mentioned in the chapter No.8 that the Mn-deposits of the Saidgi and Shuidar area, having MnO in the range of 36 to 60 wt% and 31 to 46 wt% respectively, can be cost effective if pre-concentration studies have been conducted on these deposits. During the present research it was realized that a preliminary study in this regard should be conducted on these deposits in order to see whether manganese concentration in these deposits could be upgraded or not.

It is understood that the main use of manganese is in the steel industry which is the major consumer of manganese ore. It can also be used in batteries and chemical industries. The manganese ore required for the steel industry generally contains 48% MnO_2. However, much higher grades are required for Battery making industry (MnO_2 = 78-84wt%) and chemical industry (74-84 wt% MnO_2). Keeping these grades under consideration, these Mn-deposits can be utilized in steel making industry and are, therefore, already supplied or being supplied to the Pakistan steel industry at Karachi. The Saidgi and especially, Shuidar Mn-deposits need benificiation or upgradation before being utilized in battery and chemical industries.

During the present study two different techniques i.e., magnetic separation and gravity concentration method were used for the upgradation of Saidgi Mn-ores. The detail of these techniques and the outcomes are discussed in this chapter.

The following terms will be most frequently used in the forthcoming text of this chapter. These are, therefore, briefly defined here.

a. A concentrate (C): It can be defined as the most valuable mineral or metal contents removed from the bulk material by passing through the concentration process.

b. A middling (M): It is a product of concentrating process where the assay of the target mineral or metal content is between the assays of concentrate and the feed or bulk material.

c. A tailing (T): It is product of the concentrating process where the assay value and the metal contents are so low that there could not be any possibility to get economical recovery.

d. Recovery (R): It is the ratio of the weights of the metal in the concentrate and feed. Mathematically it can be expressed as the ratio of the actual weight of concentrate multiplied by the assay of concentrate to the actual weight of metal in the feed multiplied by the assay of the feed.

e. Ratio of concentration (K): It is the mere weight ratio of the relative weight of feed and that of the concentrate.

MAGNETIC SEPARATION METHOD

Magnetic separation method is a proven means of purification and pre-concentration of mineral product. Any solid placed in magnetic field is affected by it in some way. Solids may be classified into two broad categories: (1) Diamagnetic solids which are repelled and (2) para-magnetic solids which are attracted by magnetic fields. For practical consideration, the more common magnetic solids are classified into three groups namely strongly magnetic (3) weakly magnetic and (4) non-magnetic. The art of separating one solid from another by means of magnetic field is called magnetic separation.

During this study electro-high intensity magnetic separator (Plate 15) was used to separate the non-magnetic (un-required) material from the magnetic (required) material. The high intensity magnetic seperator remove weakly magnetic particles from the feed material. In this seperator the cross belts are used which pick the magnetic material from the feed belt and discharge them to a side. In this way the separation of magnetic material from non-magnetic material is made.

GRAVITY CONCENTRATION METHOD

Gravity concentration methods separate minerals of different specific gravity by relative movement in response to gravity and one or more other forces offered by the water and air. Gravity methods of separation are used to treat variety of materials ranging from heavy material such as galena (Sp.Gr. 7.5) and light material like coal (Sp. Gr. 1.3).

In this method a shaking table is used, which is also called as Mozely table (Plate 16). In shaking table a flowing film of water flows over a flat inclined surface, which separate coarse and light particles from small dense particles. The table is vibrated longitudinally also using a slow forward stroke and a rapid return which cause the mineral particles to "Crawl" along the table parrallel to the direction of motion. The minerals are thus subjected to two forces: that due to the table motion, and that which is at right angle to it, due to the flowing film of water.

The net effect is that the particles move diagonally across the table from the feed end, and since the effect of the flowing film depend upon the size and density of the particles, they fan out on the table, the smaller denser particles riding highest towards the concentrate launder at the far end while the larger, lighter particles are washed into the tailing launder which run along the length of the table.

Plate 15 . A view of the Electro-High-Intensity magnetic separator.

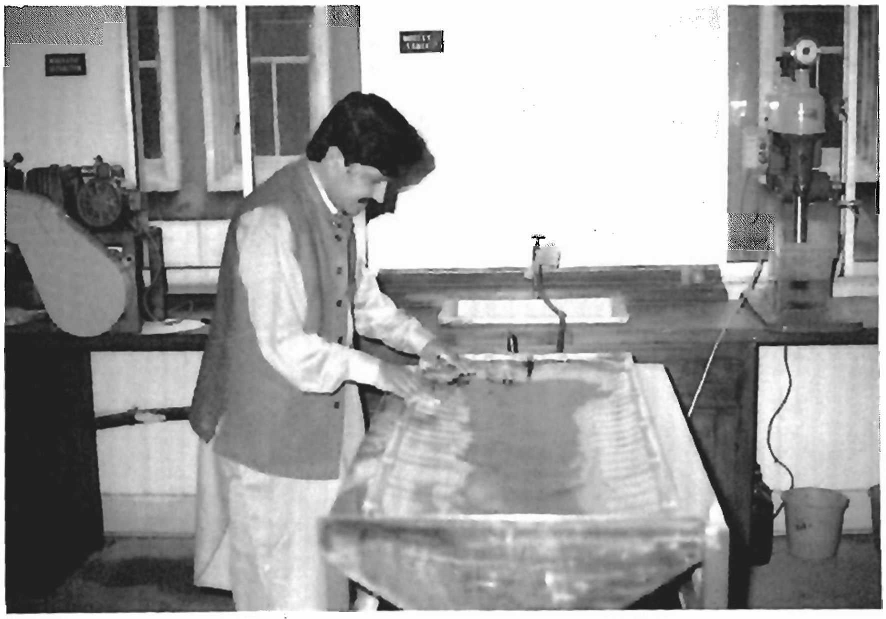


Plate 16 . A view of the Mozely shaking table.

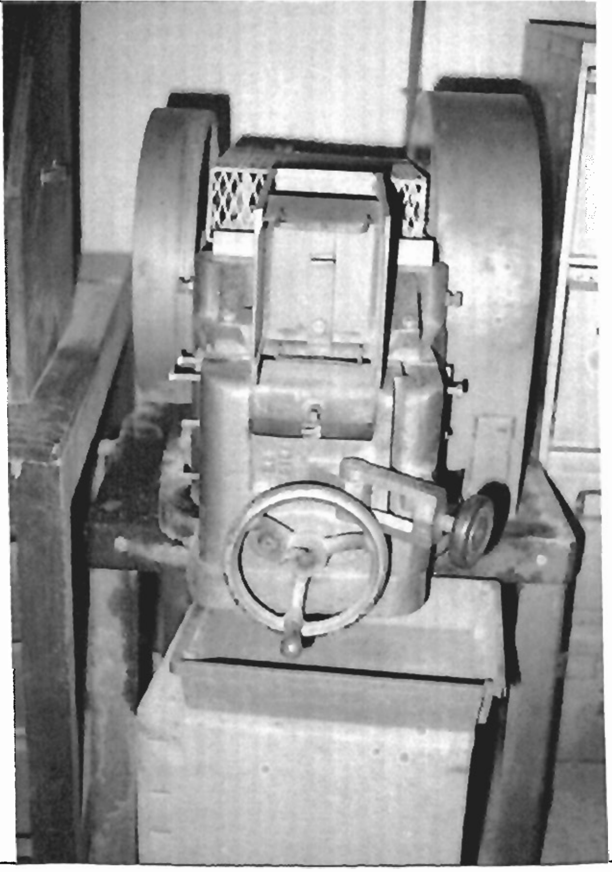
SAMPLE TREATMENT AND UPGRADATION

Two samples of different grades 37.92 and 67.36 WT% MnO_2(10 Kg each) were crushed in the laboratory scale jaw crusher (Plate 17) upto <1.8 cm size. The jaw crusher product was reduced upto 2 mm size by the role crusher (Plate 18). This product was then split further in the dry sample spliter (Plate 19) to prepare the sample for metallurgical test work programme.

1 Kg of both the samples were grinned in the rod mill (Plate 20) for up to 5 minutes. The liberation size was determined on the basis of best results of chemical analysis. The 5 minutes rod mill grinding gave positive result for concentration/upgradation at a size-100+200 #.

The -100 to +200 # size product, obtained by the automatic seive vibrating machine (Plate 21) was passed to the magnetic separator having belt speed of 1000 RPM and roll distance of 3 mm current intensity of 15-20 amp and also potential difference of 20 volts. Magnetic separator gave 3 products of each sample, (1) Concenterate (2) Middling and (3) tail. The chemical analyses of the end product were carried out by atomic absorption and results along with recovery are given in Table 6.

The -100 to +200 # product of one of the above mentioned two samples, having 67.37 wt% MnO2, was also treated by gravity concentration method by using mozely shaking table for 12 minutes. The products (concentrates and tail) were analysed by atomic absorption and the results along with recovery are given in Table 7.



Dlate 17 . A view of the Jaw crusher.

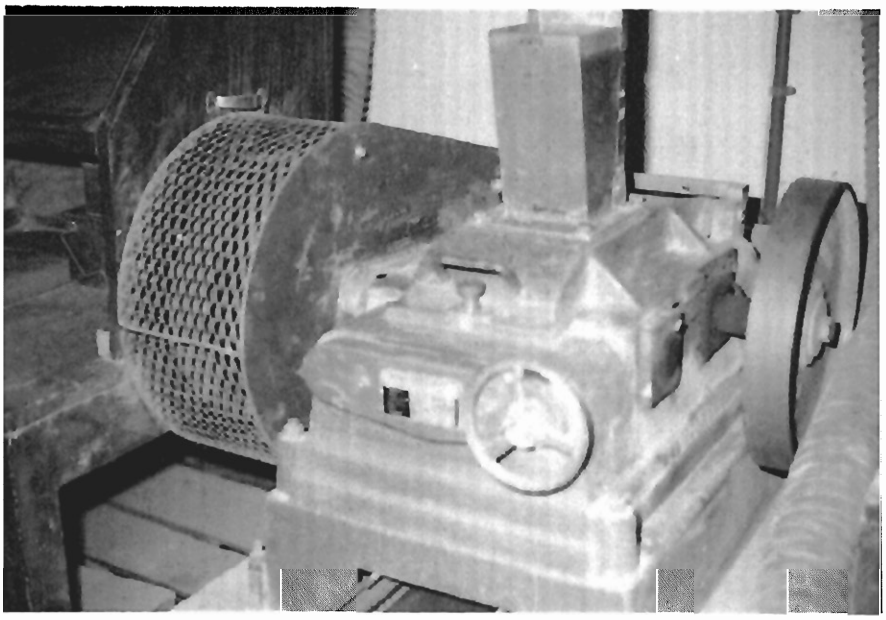


Plate 18. A view of the Roll crusher.

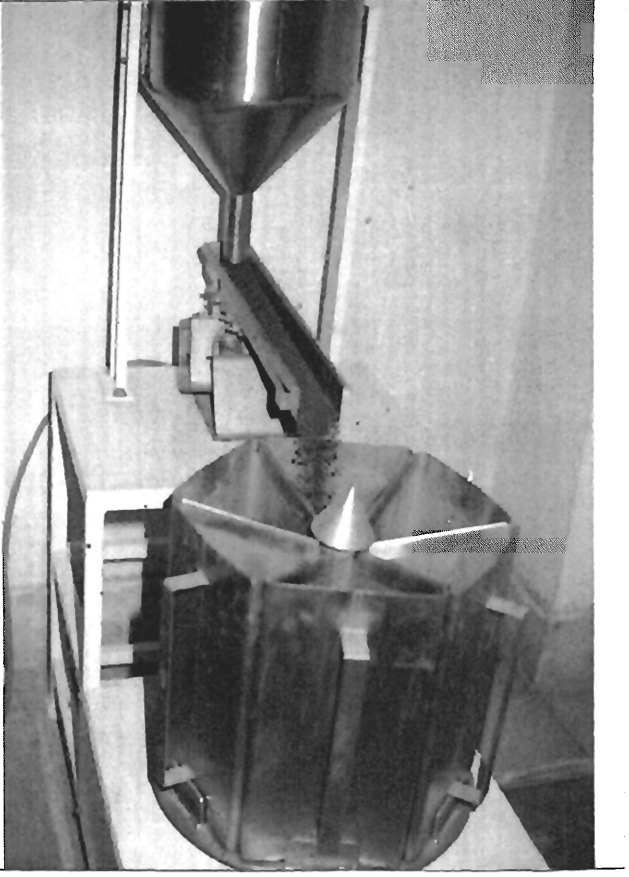


Plate 19. A view of the sample splitter.

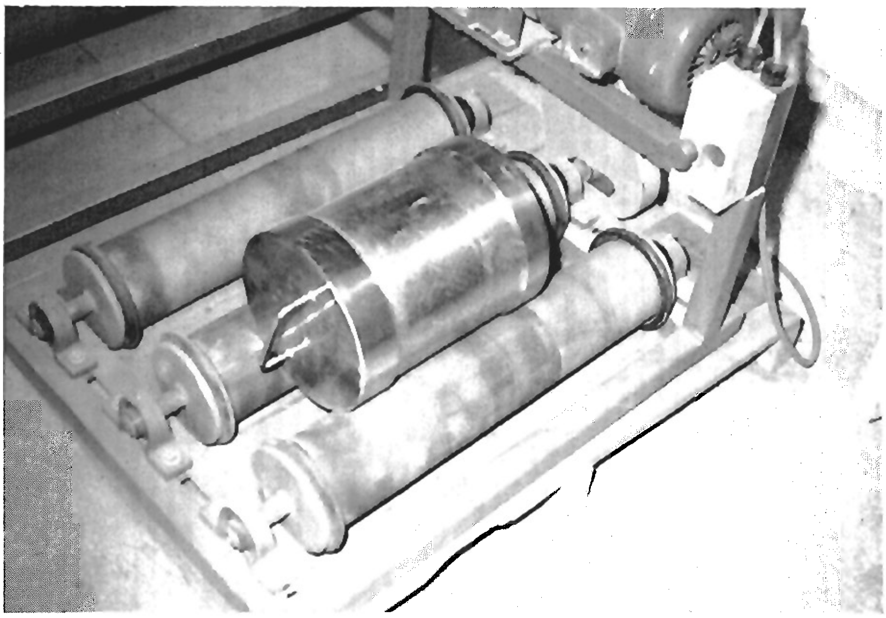


Plate 20. A view of the Rod mill.

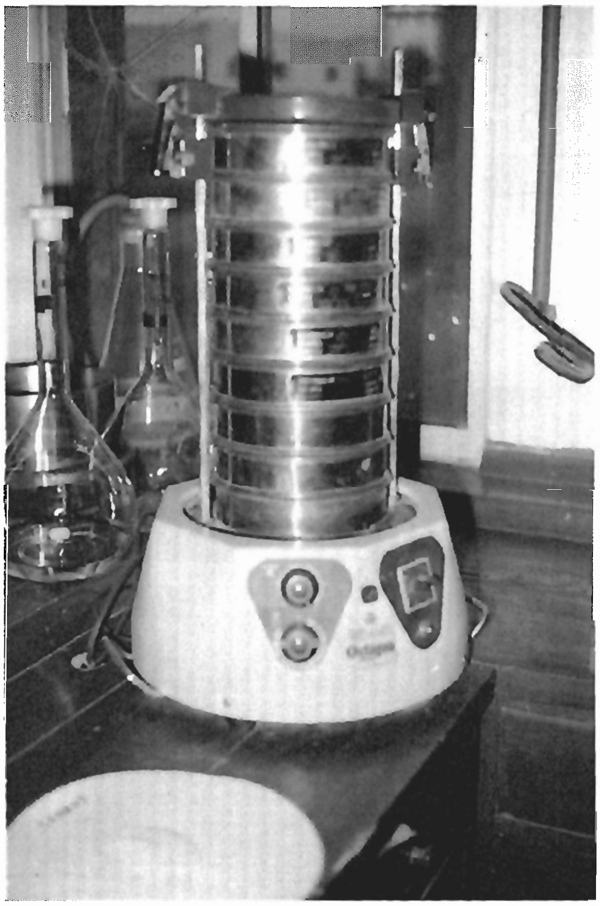


Plate 21. A view of an automatic sieve vibrating machine.

RESULTS AND DISCUSSION

One sample, having 37.98 wt% MnO2, after treatment by magnetic separator was upgraded to 60.83 wt% MnO_2 with recovery of 94.22% (Table 6). The silica in this process reduces from 57 to 12.5 wt% (table 6).

The sample, having 37.98 wt% MnO_2 (Table 6), after having treated by magnetic separator gave three products (i.e. concentrate, middling, & tail). It is clear from table- that the concentrates middling and tail have 79.00 wt%, 39.50 wt%, 22.12 wt% MnO_2 respectively. In this process the SiO_2 has been retained in the middling (47 wt%) and tail (62 wt%) (Table 18). The recovery of MnO_2 in concentrate is 94.22% while the middling and tail have very low recovery of 3.9% and 1.7% respectively.

Table 6 shows that the sample No. MB-2, having relatively higher amount of MnO_2 (67.36wt%) after treating by magnetic separator, gave similar results as that of the previous low grade ore-sample. The concentrate of this sample has been upgraded to 80.44 wt% MnO_2 and middling and tail contain 21.85 wt% and 5.36 wt% MnO_2 respectively. The recovery of MnO_2 in concentrate of this sample has been calculated as 98.26%. The middling and tail have low recovery of 1.19% and 0.55% respectively.

After treating these two samples by the method of magnetic separator it has been concluded that the Mn-deposits of Saidgi area can very easily be upgraded with a very high recovery (94%) for battery and chemical grade by the simple technique of magnetic separation.

Table 7 shows the results of one of the sample (MB-2) which has been treated by a gravity method. It is clear from this table that the concentrate has 72.19 wt% MnO_2 with a maximum recovery of 84.77%. The tail has 59.55 wt% MnO_2 with a recovery of 15.23% (Table 7). This method has upgraded the ore upto about 5%.

Table 6. Upgradation of two Mn ore samples of Saidgi area, north Waziristan by magnatic separation method.

Sample No. MB-1		---------Assay after treatment---------			---Recovery after treatment------		
	Feed assay	Concentrate	Middling	Tail	Concentrate	Middling	Tail
Wt(g)	-	217.6	18.4	14.6	-	-	-
Wt(%)	-	86.76	7.34	5.9	-	-	-
MnO2	37.98	60.83	39.5	22.12	94.22	3.99	1.79
SiO2	57	12.5	47	62	60.41	19.22	20.38
Al2O3	0.23	3.5	4	3.8	85.43	8.26	6.31
K2O	0.3	0.22	0.33	0.32	81.58	10.35	8.07
Na2O	0.8	0.67	0.74	0.72	85.73	8.01	6.26

Sample No. MB-2		---------Assay after treatment---------			---Recovery after treatment------		
	Feed assay	Concentrate	Middling	Tail	Concentrate	Middling	Tail
Wt(g)	-	127.6	9.7	10.7	-	-	-
Wt(%)	-	88.61	3.96	7.43	-	-	-
MnO2	67.36	80.44	21.85	5.36	98.26	1.19	0.55
Fe2O3	0.8	0.78	1.33	1.05	84.1	6.41	9.49

Table 7. Upgradation of one Mn ore sample of Saidgi area, north Waziristan by gravity seperation method.

Sample No. MB-2

	Feed assay	--Assay after treatment--		--Recovery after treatment--	
		Concentrate	Tail	Concentrate	Tail
Wt(g)	-	174.5	38	-	-
Wt(%)	-	82.12	17.88	-	-
MnO2	67.36	72.19	48.95	84.77	15.23
Fe2O3	0.8	0.84	0.88	81.43	18.57

By comparing the two methods (magnetic separation and gravity method) it can be concluded that the magnetic separation method is an appropriate method for the benification of the Mn-ore deposits of Saidgi and Shuidar areas of North Waziristan.

CONCLUSIONS

- North Waziristan is dominantly composed of the rocks of the waziristan ophiolite complex, Indian plate and quaternary deposits.

- Ophiolite Complex is generally composed of ultramafics, gabbros, sheeted dikes, pillow lavas, pelagic sediments and plagiogranites.

- The rocks of the Indian plate are mainly limestone, shale and sandstone of jurassic to Cretaceous age.

- The saidgi and shuidar Mn-deposits,hosted by metacherts, occur within the Waziristan ophiolite complex.

- In saidgi area the ore bodies are generally massive while that of shuidar are banded in appearance.

- The metacherts are finely crystalline, thin to medium bedded hard rocks, generally overlying the metavolcanics (pillow basalt).

- Braunite (only Mn-bearing phase) and cryptocrystalline quartz are the main constituents along with minor hematite, chalcedony and pseudomorphs of radiolarian tests.

- The chemistry of braunite has similarity with the natural braunite and also with that of the Mn-deposit found in ophiolite sequences else where in the world.

- Chemically the Saidgi Mn-deposit have higher MnO and lesser SiO_2 and Fe_2O_3 as compare to that of shuidar Mn-deposits. Both these deposits are characterized by low Fe/Mn ratio.

- Major and trace element data suggest hydrothermal origin for these Mn-deposits and show no any relation with hydrogenous deposits.

- Metacherts of Saidgi and Shuidar area have same mineralogical and chemical characteristics and favour their formation by the submarine effusive process.

- Both saidgi and Shuidar Mn-deposit are spatially separated from each other but are co-genetic. These are formed by the sub-marine hydrothermal solution in an ocean floor spreading environment within the Neo-Tethy ocean. These deposits are therefore, originated along sea floor spreading Centers (Mid-ocean ridges) and are latter on abducted on land along with the other ophiolitic rocks of the area.

- Economically the saidgi Mn-deposits are of greater importance as compare to the Shuidar Mn deposit and can be used for many industrial purposes.

- The benificiation studies of the Saidgi Mn-deposits suggest that these can be upgraded to batteries and chemical grade.

APPENDIX

METHODOLOGY/ANALYTICAL TECHNIQUES

All the techniques were performed at various laboratories of the National Centre of Excellence in Geology, University of Peshawar.

QUALITATIVE AND QUANTITATIVE MINERAL ANALYSES METHODS

Rock samples collected during field were treated for preparing thin sections (both polished and un-polished) for silicate and ore mineralogy. The silicate mineralogy has been carried out by Nickon plane polarized microscope while the ore mineralogy has been carried out by the Nickon metallurgical microscope. The qualitative ore mineralogy has also been carried out by the Rigco X-ray Differactometer powder pattern and the minerals have been identified by the d-spacing values. The chemical analyses of braunite phase have been determined by using the Jeol Electron Microprobe.

WHOLE ROCK GEOCHEMICAL ANALYSES

CRUSHING OF ROCK SAMPLES

Samples of both manganese ore and metachert collected during field from the study area were thoroughly checked for their extensive alteration and weathering. Representative samples were then selected for further experimental work. The rock samples were crushed in Jaw crusher and then the crushed chips were pulverized in a tungsten carbide ball mill to 200 mesh size. A portion of individual sample was collected after proper quartering and coning. During this whole process greater care was practiced to avoid contamination. The powdered samples were stored in the air tight glass bottles. These bottles, after removing the lids, were kept in the oven at 110 °C for two hours in order to remove the moisture.

PREPARATION OF STOCK SOLUTIONS

The moisture free powders of the manganese ores, metacherts as well as the world known rock standards were dissolved in to stock solutions of known volume by different methods. These stock solutions were used for the determination of major, minor and trace elements by classical and instrumental methods.

1.Stock Solution A

HF and $HClO_4$ digestion method: 0.5g of powdered rock sample was accurately weighed in a platinum crucible and was moist with few drops of deionized water and 5 drops of $HClO_4$. Then 10 ml of concentrated (49%) HF was added and heated on a sand bath to break down clay minerals and to drive off all silica as SiF_4 . The solution is evaporated and dried. The crucible was then removed from the sand bath and was cooled for few minutes. Five additional drops of $HClO_4$ were added and was again kept on sand bath until dry residue was obtained. The residue was then dissolved in 10 ml HCl and again heated for a while and is then diluted to about 20 ml with distilled water. The solution was kept hot and transfered to 100 ml flask for the final dilution. This procedure prevented the formation of colorless precipitates occasionally produced by Fe-rich samples when the solution came in contact with the cold flask. All the samples were treated by the same procedure for the preparation of solution A. This solution was kept for the determination of all the major oxides, minor and trace elements except SiO_2 and Al_2O_3 in both managanese ore and metacherts.

2. Stock Solution B

Sodium hydroxide fusion method: 30 g of NaOH pellets were dissolved in 100 ml deionized water and stored in a polythene bottle. 5 ml aliquots of NaOH solution was added to a series of already cleaned nickle crucibles. The crucibles were kept on hot plate at approximately 100 C^{O} for complete dryness. These were then cooled in a desicator. Accurately weighed 0.05g of rock samples and certified rock Standards were added to separate crucibles. One crucible was used for the preparation of blank. The crucibles were covered with lids and each crucible was heated to dull redness over a gas burner for a period of 5 minutes. The crucibles were swirled while hot. Deionized water (5-10ml) was added to each crucible. The contents of each crucible were washed into different 600 ml polythene beakers which already contained 400 ml of deionized water and 10 ml of concentrated HCl. In most cases clear solution was obtained at this stage. However, in few cases the solution was not clear. This type of solution was then warmed until the clear solution was obtained. The resulting solution was transferred to one litre volumetric flask and was made to the volume with deionized water and stored in polythene bottles for the determination of silica and alumina. This solution was used for the determination of SiO2 and Al2O3 in both Mn-ores and metacherts.

DETERMINATION OF MAJOR AND MINOR OXIDES

DETERMINATION OF SiO_2

Spectrophotometric method

The method by Shapiro and Brannock in the book "Chemical Methods of Rock Analysis" by Jeffery (1987) was adopted. In this method the silica in the solution B is determined by reducing the yellow colour of silico molybdate to blue colour.

Instrument: SP8-400 PYE UNICAM UV/VIS spectrophotometer.

Reagents

1. **Ammonium molybdate solution:** 7.5g of ammonium molybdate was dissolved in 70 ml deionized water by adding 20 ml of 9 N H_2SO_4. The solution was made to the volume of 100 ml and was stored in a polythene bottle.

2. **Tartaric acid solution:** 25g of the tartaric acid was dissolved in deionized water and was diluted to 250 ml with deionized water.

3. **Reducing solution:** 0.7g of sodium sulfite Na_2SO_3, 0.15g of 1-amino-2-naphthol-4-sulphonic acid and 9g of sodium metabisulfite ($Na_2 S_2O_5$) was dissolved in 100 ml of deionized water. The solution was kept in a cool and dark place and was prepared freshly as this solution deteriorate after few days.

Procedure: 10 ml of stock solution B of each of the Mn-ores, metachert and each rock standards and a blank was taken in a series of 100 ml volumetric flasks. About 50 ml of deionized water was added to each flask. 2 ml of ammonium molybdate solution was added to each flask and was swirled to mix well. After exactly 10 minutes, 4 ml of tartaric acid solution was added to each flask and again swirled and mixed well. At the end 1 ml of reducing solution was added to these flasks and each flask was diluted to 100 ml with deionized water. All these solutions were set aside for at least 30 minutes. Blue color solution was obtained at the end. The silica determination was then made on the spectrophotometer at a wavelength of 650nm relative to the reference rock standards.

DETERMINATION OF $Al_2 O_3$

Spectrophotometric Method

Instrument: SP8-400 PYE UNICAM UV/Visible spectrophotometer

Reagents

1. **8-hydroxyquinoline solution:** 1.25g of the 8-hydroxyquinoline was dissolved in 250 ml of pure grade of chloroform and was stored in a refrigerator.

2. **Complexing reagent:** 1g of hydroxylamine hydrochloride ($HONH_2HCl$), 3.6g of sodium acetate trihydrate and 0.4g of berillium sulphate tetrahydrate were dissolved in 50 ml of deionized water. 0.04g of 2,2 dipyridyl was also dissolved in 20 ml of 0.2N HCl. Both the solutions were then mixed and diluted upto 100 ml with deionized water.

Procedure: 5 ml of each stock solution B of Mn-ores, metachert and 3 known standards and a reagent blank were taken into a series of 100 ml seperatory funnels. 5 ml of deionized water and 10 ml of complexing reagent solution were added to these funnels and mixed well. After few minutes 20 ml of 8-hydroxyquinoline solution was added to each funnel. These solutions were then shaked for about 8 minutes by an automated flask shaker. The organic layers obtained at the bottom of these solutions in the seperatory funnels were then separated into 25 ml volumetric flasks by washing the funnels with chloroform for several times. The final volume of 25 ml for each sample was made with chloroform. The yellow color extracts obtained through this process were suitable for spetrophotometric determination. The Al_2O_3 was determined at wavelength of 381 nm relative to the reference rock standards according to the method of Riley (1958).

DETERMINATION OF TOTAL IRON

The total iron as Fe_2O_3 in the studied rock samples was determined by atomic absorption spectrophotometer by using the stock solutions A.

Instrumental conditions

Mode	Absorption
Wavelength	248.3 nm
Slit width	0.2 nm
Air flow	5litre/minute
Fuel flow	1litre/minute
Burner hight	10 mm

1. Stock solution of 1000 ppm for Fe: I gram of pure iron metal was dissolved in minimum amount of HCl and was made to the volume with deionized water in one litre volumetric flask.

2. Stock solution of 100 ppm: 10 ml from 1000 ppm stock solution was taken in 100 ml volumetric flask and made to the mark with deionized water.

3: Working standard solutions: 1, 2, 4 and 8 ppm working standard solutions were prepared by taking 1, 2, 4 and 8 ml from the 100 ppm stock standard solution in a 100 ml volumetric flask and made to the volume with deionized water.

Procedure: The atomic absorption spectrophotometer was set according to the above conditions. The instrument was calibrated with the iron working standard solutions of 4 and 8 ppm. The working standards 1, 2, 4 & 8 ppm were then run as unknown. After verification of accuracy, the stock solutions A of both certified rock standards and samples were run on the machine. The results were compared with the certified values and were found within the confidence limit. After making sure that the instrument is properly calibrated the rest of the sample solutions were run on the atomic absorption and the results of iron as Fe_2O_3 were determined.

DETERMINATION OF CaO AND MgO

The CaO and MgO in both the certified rock standards and the studied ores and metacherts were determined by atomic absorption spectrophotometric method by using the stock solutions A.

Instrument: SP 191 PYE UNICAM Atomic Absorption Spectrophotometer

Instrument conditions:

Element	Ca	Mg
Mode	Absorption	Absorption
Wavelength	422 nm	285.2nm
slit width	0.4nm	0.4nm
Air flow	5l/min	5 l/min
Fuel flow	5 l/min	To best flame
Burner hight	10mm	10mm

1. Stock solution of 1000 ppm for Ca & Mg: 2.497g $CaCO_3$ and 3.057g $MgCO_3$ were dissolved in 1N HCl and was diluted to one litre with deionized water in a 1000 ml volumetric flask.

2: Stock solution of 100 ppm for Ca & Mg: 10 ml of 1000 ppm stock solution was taken in 100 ml volumetric flask and was made upto the mark with deionized water.

3: Lanthanum 5% Solution: 58.64g of La_2O_3 was dissolved in 200 ml deionized water to which 150 ml 60 % $HClO_4$ was added. It was heated until complete dissolution. The solution was then filtered through ordinary filter paper into 1000 ml volumetric flask and the volume was made upto the mark with deionized water.

4. Working Standards: 1, 2, 4 and 8 ppm of working standards for Ca and Mg were prepared by taking 0.5, 1, 2 and 4 ml of 100 ppm stock solution in a series of 50 ml volumetric flasks. To these flasks 10 ml lanthanum solution was added and the volume was made upto the mark with deionized water.

5. Dilution of Samples: 5 ml (depending upon the expected concentration of Ca & Mg) of the stock solution A of both certified rock standards and the studied rock samples were taken in a series of 50 ml volumetric flasks. 10 ml of lanthanum solution was added to each flask and the volume was made to the mark.

Procedure: Atomic absorption spectrophotometer was set according to the above mentioned conditions for Ca and Mg separately. The cathode lamp for both Ca and Mg were turn ON to warm up for at least 10 minutes. The instrument was then calibrated and standardized with the working standards of 2 and 4 ppm. All the working standards were run as unknown and their actual concentration was verified. For further accuracy the certified rock standards were run as unknown and the results were compared. After making sure that the results of the certified standards were within the confidence limit, the studied rock sample solutions (in diluted form) were run on the atomic absorption and the concentrations of Ca and Mg were noted for each sample. The wt% of CaO and MgO in each sample was then calculated.

DETERMINATION OF $Na_2O + K_2O$

Both Na_2O and K_2O were determined by atomic absorption spectrophotometer by using the stock solutions A.

Instrument: SP 191 PYE UNICAM atomic absorption spectrophotometer

Instrument Conditions:

Element	Na	K
Mode	Emission	Emission
Wavelength	589 nm	766 nm
Slit width	0.2 nm	0.4 nm

Air flow	5 l/min	5 l/min
Fuel flow	1 l/min	1 l/min
Burner hight	20 mm	20 mm

1. Stock solution of 1000 PPM for Na & K: 3.087 g moisture free Na_2SO_4 and 2.228g moisture free K_2SO_4 were dissolved in deionized water and the volume was made to 1000 ml in a volumetric flask. The solution was stored in a polythene bottle.

2. Stock solution of 100 PPM Na & K: 10 ml of 1000 PPM stock solution was taken in a 100 ml flask and diluted to mark with deionized water.

3. Working Standards: 1, 2, 4 and 8 ppm working standards were prepared by taking 1, 2, 4, and 8 ml from 100 PPm stock solution in 100 ml volumetric flasks and was diluted up to the mark with deionized water.

4. Diluted samples: All the samples as well as certified rock standards were diluted to 20 times.

Procedure: The atomic absorption spectrophotometer was set according to the above mentioned instrumental conditions in order to get the maximum absorbance. The instrument was set on emission mode and a conical burner head was used. In this case no cathode lamp was required. The instrument was calibrated and standardized by working standards of 4 and 8 ppm and then the working standards were also run as unknown in order to verify the standardization of the instrument. The diluted certified rock standards were then run and the results were compared to know the accuracy of the method. The diluted solutions of rock sample were sprayed one by one through the flame and the concentration of Na and K was noted in each sample. The wt% of Na_2O and K_2O were then calculated.

DETERMINATION OF MnO

MnO in the studied rock samples was determined by atomic absorption by using the stock solutions A & B.

Instrument: SP 191 PYE UNICAM atomic absorption spectrophotometer

Instrument conditions:

Mode	Absorption
Wave length	279.5nm
Slit width	0.2nm
Fuel flow	1 l/min
Air flow	5 l/min
Burner hight	10mm

1:Stock solution of 1000 ppm for Mn: 4.058g of $MnSO_4.4H_2O$ was dissolved in 20 ml of 1N H_2SO_4. It was then transferred to 1000 ml volumetric flask and was made upto the mark with deionized water.

2: Stock solution of 100 ppm: 10 ml of 1000 ppm stock solution was taken in 100ml volumetric flask and was made upto the volume with deionized water.

3: Working standards: 1, 2, 4 and 8 ppm working standards of Mn were prepared by taking 1 2, 4 and 8 ml of 100 ppm stock solution in a 100ml volumetric flask and was made to volume with deionized water.

Procedure: The atomic absorption spectrophotometer was set according to the above mentioned conditions and the cathode lamp for Mn was warmed up for 10 minutes. After warming up of the cathode lamp the instrument was calibrated and standardized with the working standards. The stock solutions of certified rock standards were then run to check the accuracy of the method. After making sure that the atomic absorption is calibrated properly, solution A of the unknown samples were sprayed into the flame and the concentration of Mn was noted for every samples. The wt% of MnO was then calculated.

DETERMINATION OF TiO_2

TiO_2 in the studied samples was determined by spectrophotometric method by using the stock solution A.

Instrument: SP8-400 PYE UNICAM UV/VIS spectrophotometer

Procedure: 10 ml of stock solution A of the ores and metacherts respectively and at least two certified rock standards were taken in 50 ml volumetric flask. Few drops of H_3PO_4 and 2 ml of H_2O_2 were added to each flask. The solution in each flask was made to volume with 10 % H_2SO_4 solution. A blank sample was also prepared by the same method. These solutions were then shaked and mixed well and were ready for analysis. The spectrophotometer was turn ON and set to warm up for 30 minutes. The wave length optimization was done on the certified rock standards. A maximum peak was noticed at 445 nm. The instrument was set on a wavelength of 445 nm and was zeroed with the blank. The certified rock standards were run on the instrument and the results were calculated and compared with the certified values. After making sure that the results of the certified standards were within the confidence limit, the rock sample solutions were then run as unknown. The optical density of each sample was noted and the wt% of TiO_2 for each sample was then calculated.

DETERMINATION OF P_2O_5:

P2O5 in the studied samples was determined by spectrophotometric method by using the stock solution A.

Instrument: SP8-400 PYE UNICAM UV/VIS spectrophotometer.

Reagents:

1: Ammonium meta vanadate solution: 0.25g ammonium meta vanadate (NH_4VO_3) was dissolved in 120 ml of 33% HNO_3.

2. Ammonium molybdate solution: 10 g of ammonium molybdate was dissolved in 80 ml of deionized water.
Both the solutions were mixed and stored in polythene bottle.This mixture is used as vanadate molybdate reagent.

Procedure: 10 ml of stock solution A of ores and metacherts and at least two certified standards were taken in series of 50 ml volumetric flasks. To each flask 2 ml of vanadate molybdate reagent was added. The volume was made to the mark with deionized water. The solutions were shaked and were run on spectrophatometer as under: The spectrophotometer was turn ON and set to warm up for 30 minutes. The wave length optimization was done on the certified rock standards. A maximum peak was noticed at 372 nm. The instrument was set at 372 nm and was zeroed with the blank. The certified rock standards were run on the instrument and the results were calculated and compared with the certified values. After making sure that the results of the certified standards were within the confidence limit, the rock sample solutions were then run as unknown. The optical density of each sample was noted and the wt% of P_2O_5 for each sample was then calculated.

DETERMINATION OF IGNITION LOSS

Gravimetric method

Sample of known weight were taken in already weighed porcelene crucibls. These crucibles along with the samples were kept in a furnace at 1000 C^O for 3 hours. Then cooled in a desicator and weighed after 15 minutes. The difference in weight was noted and the amount of ignition loss (in percent) was calcululted for each sample.

DETERMINATION OF TRACE ELEMENTS

DETERMINATION OF NICKLE (Ni)

Atomic absorption spectrophtometer method

Instrument: SP 191 PYE UNICAM Atomic Absorption spectrophotometer

Instrument conditions:

Mode	Absorption
Wavelength	232nm
Slit width	0.2nm
Fuel flow	1 l/min
Air flow	5 l/min

1: Standard stock solution of 1000 ppm: 1g of Ni metal was dissolved in a minimum volume of(1:1) HNO_3 and was diluted to 1 litre with deionized water.

2. Standard stock solution of 100 ppm: 10ml from 1000 ppm stock standard solution was transferred into a 100 ml volumetric flask and was made to the mark with deionized water.

3: Working standards: 0.5, 1, 2, 4 ppm standard solution were prepared by taking 0.5, 1, 2 and 4 ml from 100 ppm standard solution into a series of 100 ml volumetric flasks and was made to the mark with deionized water.

Procedure: The atomic absorption spectrophotometer was set according to the above mentioned conditions. Ni cathode lamp was turned ON and allowed to warm up for 10 minutes. After warming up of cathode lamp, the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 2 and 4 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution of certified standards was run and the results were compared with the certified values. After making sure that the result of the certified standards were within the confidence limit, the sample's stock solutions A were then aspired into the flame and the Ni concentration of each sample was noted. The Ni contents in ppm were calculated according.

DETERMINATION OF CHROMIUM (Cr)

Atomic Absorption method

Instrument: SP-191 PYE UNICAM Atomic Absorption Spectrophotometer

Instrument conditions

Mode	absorbence
Wave length	357.9nm
Slit width	0.2nm
Fuel flow	4.5 l/min
Air flow	5.0 l/min

1: Standard stock solution of 1000 ppm: 3.735g of K_2CrO_4 was dissolved in deionized water and diluted to one litre with deionized water.

2. Standard stock solution of 100 ppm: 10ml of 1000ppm standard stock solution was taken in 100 ml volumetric flask and was made to the mark with deionized water.

3. Working standards: 0.5, 1, 2, 4 and 8 ppm of working standards
were prepared by taking 0.5, 1, 2, 4 and 8 ml from the standard stock solution of 100 ppm in a 100ml volumetric flask and was made to the mark with deionized water.

Procedure: The atomic absorption spectrophotometer was set according to the above mentioned conditions. Cr cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 4 and 8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution C of certified standards were run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards were within the confidence limit, the sample's stock solutions A were then aspired into the flame and the Cr concentration of each sample was noted. The Cr contents in ppm were calculated.

DETERMINATION OF COBALT (Co)

Atomic absorption method:

Instrument:SP 191 PYE UNICAM Atomic Absorption Spectrophotometer.

Instrument conditions:

Mode	Absorption
Wave length	240.7 nm
Slit width	0.4 nm
Fuel flow	1.2 l/min
Air flow	5 l/min
Burner height	10 mm

1: Standard stock solution of 1000 ppm: 1.0 g of cobalt metal was dissolved in 30 ml of (1:1) HCl and was diluted to one litre with deionized water.

2. Standard stock solution of 100 ppm: 10ml of 1000 ppm stock solution was taken in 100 ml volumetric flask and was made to the mark with deionized water.

3. Working standards: 0.5, 1, 2, 4 and 8 ppm of working standards were prepared by taking 0.5, 1, 2, 4 and 8 ml from 100 ppm standard stock solution in a series of 100 ml volumetric flasks and made to the mark with deionized water.

Procedure: The atomic absorption spectrophotometer was set according to the above mentioned conditions. Co cathode lamp was turned ON and let it to warm for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 4 and 8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution of certified standards were run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards were within the confidence limit, the sample stock solutions A were then aspired into the flame and the Co concentration of each sample was noted. The Co contents in ppm were calculated.

DETERMINATION OF COPPER (Cu)

Atomic Absorption method

Instrument: SP 191 PYE UNICAM atomic absorption spectrophotometer.

Instrument conditions

Mode	Absorption
Wave length	325.8nm
Slit width	0.4nm

Fuel flow	1 l/min
Air flow	5 l/min
Burner height	10 mm

1. **Standard stock solution of 1000 ppm:** 1 g of copper metal was dissolved in 30 ml of (1:1) HNO_3 and was made to the volume of one litre with deionized water.
2. **Standard stock solution of 100 ppm:** 10 ml of 1000 ppm standard stock solution was taken in 100 ml volumetric flask and was made to the mark with deionized water.

3. **Working standards:** 0.5, 1, 2, 4 and 8 ppm of working standards were prepared by taking 0.5, 1, 2, 4, and 8 ml from 100 ppm standard stock solution into a series of 100 ml volumetric flasks and made to the volume with deionized water.

Procedure: The atomic absorption spectrophotometer was set according to the above mentioned conditions. Cu cathode lamp was turned ON and let it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 4 and 8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution A of certified standards were run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards were within the confidence limit, the sample stock solutions A were then aspired into the flame and the Co concentration of each sample was noted. The Co contents in ppm were calculated.

DETERMINATION OF LEAD (Pb)

Atomic absorption method:

Instrument: SP 191 PYE UNICAM Atomic Absorption Spectrophotometer.

Instrument conditions:

mode	absorption
Wavelength	217 nm
Slit width	0.4 nm
Fuel flow	1 l/min
Air flow	5 l/min
Burner height	10 mm

1. **Standard stock solution of 1000 ppm:** 1.598 g of lead nitrate $Pb(NO_3)_2$ was dissolved in 1% HNO_3 and was diluted to 1 litre with deionized water.

2. **Standard stock solution of 100 ppm:** 10 ml of 1000 ppm standard stock solution was taken in 100 ml volumetric flask and was made to the volume with deionized water.

3. **Working standard solutions:** 0.5, 1, 2, 4 and 8 ppm of working standards were prepared by taking 0.5, 1, 2, 4 and 8 ml of 100 ppm stock solution in a series of 100 ml volumetric flask and volume was made to the mark with deionized water.

Procedure: The atomic absorption spectrophotometer was set according to the above mentioned conditions. Pb cathode lamp was turned ON and allowed to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 4 and 8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution A of certified standards were run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards were within the confidence limit, the sample stock solutions A were then aspired into the flame and the Pb concentration of each sample was noted. The Pb contents in ppm were calculated.

DETERMINATION OF ZINC (Zn)

Atomic absorption method:

Instrument: SP 191 PYE UNICAM Atomic Absorption Spectrophotometer

Instrument conditions:

Mode	Absorption
Wavelength	213.9nm
Slit width	0.4nm
Fuel flow	1 l/min
Air flow	5 l/min
Burner height	10 mm

1. Standard stock solution of 1000 ppm: 1 g zinc metal was dissolved in about 20 ml of (1:1) HCl and was diluted to 1 litre with deionized water.

2. Standard stock solution of 100 ppm: 10 ml of 1000 ppm standard stock solution was taken in 100 ml volumetric flask and was made to the volume with deionized water.

3. Working standard solution: 1, 2, 4 and 8 ppm working standard solutions were prepared by taking 1, 2, 4 and 8 ml of 100 ppm standard stock solution in a series of 100 ml volumetric flasks. The volume in each flask was made up to the mark with deionized water.

Procedure: The atomic absorption spectrophotometer was set according to the above mentioned conditions. Zn cathode lamp was turned ON and allowed it to warm up for 10 minutes. After warming up of cathode lamp the air acetylene flame was ignited. The instrument was calibrated and standardized with working standards of 4 and 8 ppm. All the working standards were then run as unknown to verify the standardization. Stock solution A of certified standards were run through the instrument and the results were compared with the certified values. After making sure that the results of the certified standards were within the confidence limit, the sample stock solutions A were then aspired into the flame and the Zn concentration of each sample was noted. The Zn contents in ppm were calculated.

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