Chapter VI
MINERALOGIC STUDY OF THE IRON
AND ASSOCIATED MANGANESE ORES

GENERAL STATEMENT

So far no mineralogic study of the iron ores as well as the associated manganese ores of Bicholim and Sanquelim have been made by any one of the earlier workers. The author (1965) had earlier studied the mineralogy of the iron and manganese ores of the Sanguem district of South Goa. Fermor (1909), however, gave a very brief account of the lateritic manganese ores of Goa but so far as the iron ores are concerned, no such account is available to date. In course of the present investigation the author, therefore, availed of the first opportunity to examine in detail the iron and the associated lateritic manganese ores of Bicholim and Sanquelim in north Goa.

The workable deposits of iron ores of Bicholim and Sanquelim occur along well-defined zones. Small and scattered pockets of lateritic manganese ores occur rather infrequently in these deposits particularly, in the hard laminated iron ores.

As far as possible all the available types of iron ore samples representing lateritic, hard laminated and friable were collected systematically from the different sections of open cast mines of Bicholim and Sanquelim. Some difficulty were encountered in preparing the polished blocks of some soft and friable specimens, which required continuous cooking in canada balsam before they were finally polished. The powdery ore was mounted on bakelite
block for this study. About 60 representative samples of iron ores including a few manganese ores from the area have been finally selected for ore-microscopic study.

Through mineragraphic study an attempt was made to identify the ore minerals and their assemblages, state of oxidation, and finally, their textural relations and paragenetic sequence.

MINERALOGICAL DESCRIPTION

The mineralogical description of various iron and manganese minerals, which are identified in polished sections under reflected light, are given below along with their characteristic physical characters. Chemical formulae of the iron and manganese minerals are adopted after Deer, Howie and Zussman (1962), and Hewett and Fleischer (1960) respectively.

Iron Ores

Hematite \((\text{Fe}_2\text{O}_3)\).—The name hematite was first proposed by Theophrastus in 315 B.C. because of its colour resemblance to blood, for which the Greek word 'haema' was used (see Deer et al. 1962, p.21).

It occurs mostly as granular or platy crystal aggregates. Colour - dark grey, occasionally with shining crystals; lustre-metallic; streak-cherry-red; hardness - 5.5 - 6.5.

Ore-microscopic study shows that the mineral is euhedral to subhedral martite, a pseudomorph of hematite after magnetite (Plate X, fig.3) or specular or platy hematite (Plate X, fig.4).
Colour - white or greyish white usually with a bluish tone. Reflectivity - high, highest of all iron minerals. Martite shows greyish white colour, slightly lower reflectivity and weaker anisotropism than specular or platy hematite. A plausible reason for this difference in reflectivity and anisotropism may possibly be due to the presence of ferrous oxide i.e., submicroscopic residuals of magnetite scattered in martite besides incipient hydration in it (see Brokerick, 1919, p.363; Gilbert, 1925, p.592).

Etch reaction:

Negative - To all standard reagent. In a few cases HF acid reveals grain boundaries.

**Magnetite** \(\text{Fe}^{2+} \text{Fe}^{3+}_2 \text{O}_4\) - The mineral is either named after the locality Magnesia, bordering Macedonia or after Magnes who first discovered it (see Dana 1962, p.492).

The mineral is crystalline and belongs to the isometric system. Colour - steel grey to iron black; streak - black; lustre - metallic; hardness - 5.5 - 6.5.

Under reflected light the granular crystals of magnetite occur as subhedral to euhedral cubes and octahedra (Plate XI, fig.1). Incomplete martitisation of magnetite is almost a universal feature among the ores. Colour - pale grey with distinct brownish or pinkish tinge, Reflectivity - moderate, lower than hematite but higher than goethite. Isotropic.
Etch Reaction:

Positive - \( \text{SnCl}_2 \text{(Sat)} + \text{HCl} (1:1) \), develops grain boundaries. Hot HCl (1:1), darkens and solution turns yellow.

Negative - All other standard reagents.

Goethite \((\alpha - \text{FeO}.\text{OH})\). - The iron mineral goethite is named after the poet and philosopher Goethe (1749-1832 A.D., see Dana, 1962, p. 504).

The common forms in which the mineral occurs are massive, stalactitic or botryoidal. Colour - yellowish, brownish or brownish black; streak - yellow, brown; lustre - adamantine; hardness - 5 - 5.5.

Under reflected light goethite is usually massive or cryptocrystalline, sometimes colloform and rarely fibrous. Fibrous goethite generally radiates from the free surface of colloform goethite. Colour - dark to dull grey. Reflectivity - low. Anisotropic. Reflection pleochroism - weak, fairly noticeable in oil but often masked by orange to red internal reflection. According to Ramdohr (1969, p. 1047) this property of goethite is variable since it depends on the content of absorbed water. Internal reflection is more conspicuous in the massive goethite.

Etch Reaction:

Positive - \( \text{SnCl}_2 + \text{HCl} (1:1) \), attacts with formation of pits and becomes stained dark brown after three minutes.

Negative - All other standard reagents.
Lepidocrocite (γ - FeO.OH). - The name lepidocrocite was given after the Greek words 'lepidos' and 'krokis', meaning scales and fibres due to its similar habits (see Deer et al. 1962, p.122).

Because of its scanty occurrence in the ores it is practically impossible to study its physical characters in hand specimens.

Lepidocrocite is of rare occurrence in the ores examined in reflected light. Very careful observation is generally required to differentiate lepidocrocite from goethite. The mineral is exclusively associated with the colloform goethite (Plate XI, fig.2). In certain cases due to complete enclosure of goethite by thin lepidocrocite rim, an 'atoll' structure is developed (Plate XI, fig.3). Colour - pale grey to greyish white, often with brownish or bluish tinge. Reflectivity - higher than goethite but lower than hematite. Pleochroism - more distinct than goethite especially in oil, usually giving reddish-brown internal reflection. Anisotropism - strong in shades of grey.

Etch Reaction :

Positive - SnCl₂ often reveals the structure.
Negative - All other standard reagents.

Manganese Ores

Pyrolusite (MnO₂). - The names pyrolusite and polianite are often confusing and remained controversial for long, though both the minerals have identical chemical composition. Ramdohr and
Schneiderhohn (1931) suggested the name polianite for the coarsely crystalline variety and restricted the term pyrolusite to the fine-grained variety (see Dunn 1936). Oroel and Pavlovitch (1931) on the other hand used the term pyrolusite for the mineral which forms a pseudomorph after manganite, and the term polianite to the crystalline variety formed directly during the process of mineral formation (see Dunn, 1936). Based on the X-ray studies Vaux (1937) concluded that both these minerals have identical crystal structure. On the above basis Uytenbogaardt (1951) described both the varieties as a pyrolusite and discarded the use of the term polianite for the crystalline variety. Ramul (1965) differentiated polianite and pyrolusite on the basis of their forms and optical characters. The present worker observed coarsely crystalline acicular (Plate XI, fig.4) and noncrystalline varieties of pyrolusite but their optical characters are almost identical, except that the anisotropism is stronger in the case of crystalline pyrolusite than in the non-crystalline one.

Pyrolusite occurs in massive, reniform to well-developed crystalline forms. It is generally associated with the lateritic manganese ores and in a few cases with the hard iron ores. Colour - steel grey to iron black, the crystalline variety has a shining surface; streak - dark black; lustre - metallic to submetallic.

In reflected light colour of the mineral is white with a distinct yellow tinge; Reflectivity - high; coarser variety
shows reflecting pleochroism particularly, in oil; Anisotropism -
strong in shades of slaty grey and light yellow. Fine-grained
varieties are feebly anisotropic.

Etch Reaction:

Positive - SnCl₂(sat), darkens immediately.
H₂SO₄ (Conc.), stains permanently.
H₂O₂ + H₂SO₄, stains permanently,
but the reaction is more rapid.

Negative - HCl, HNO₃, KOH.

Psilomelane(Ba R₂O₁₈·₂H₂O; R = Mn. Mn.) - Psilomelane is
a general name used to define two different manganese minerals
vis., psilomelane and cryptomelane. But the two manganese
minerals cannot be distinguished by their physical or optical
characters. Ramsdell (1942) by X-ray diffraction study found
that the so called 'Psilomelane' contains 60 % cryptomelane
and about 30 % psilomelane. Chemically, these two minerals
differ only in two of their minor constituents, namely, Bao and
K₂O. According to Mukharjee (1959) the powder pattern of the
so called 'psilomelane' corresponds to that of cryptomelane. The
present worker had no opportunity to differentiate between
psilomelane and cryptomelane by X-ray diffraction or by chemical
analysis. The general term 'psilomelane' is, therefore, used
in this text.

Psilomelane is generally massive or colloform. Colour -
dark steel grey; streak - brownish black; lustre - submetallic;
hardness - 6 - 6.5.
Psilomelane is of rare occurrence in the ores examined under reflected light and often associated with pyrolusite. Colour - bluish grey to greenish white. Reflectivity - higher than pyrolusite; Anisotropic in shades of grey.

Etch Reaction:

Positive - SnCl₂(sat), blackens instantaneously.

HCl, stains brown.

H₂O₃, stains light brown.

Negative - Aqua regia, KOH, HCl, FeCl₃.

MINERALOGICAL ASSEMBLAGE

On the basis of their ore-microscopic studies, the iron and associated manganese ores of Bicholim and Sanquelim have been classified into the following four mineralogical assemblages:

Iron Ore:
- Martite-Magnetite-Goethite
- Magnetite-Hematite-Martite-Goethite

Manganiferous iron Ore:
- Martite-Magnetite-Pyrolusite-Psilotmelane

Manganese Ore:
- Pyrolusite-Psilotmelane

Martite-Magnetite-Goethite Ore

The ore belonging to this assemblage is massive and hard.
laminated. It is by far the commonest of all the iron ore deposits of the area and composed largely of granular martite surrounded by goethite, which actually occupies intergranular spaces in the ores. Frequently, martite have innumerable un-replaced fragments of magnetite whose grain boundaries are very irregular. However, there/also some unaltered to slightly altered magnetite having well-defined crystal boundaries. The ore is generally of high grade containing about 62 per cent Fe.

**Magnetite-Hematite-Martite-Goethite Ore**

The ores of the above mineral assemblage are characteristically schistose and occur restrictedly in the deposits. Hematite is specular, the flakes of which due to their preferred orientation make the ore somewhat schistose. Magnetite and its pseudomorph, martite are granular and largely confined to the granulose bands which alternate with the schistose bands consisting essentially of specular hematite. Colloform or massive goethite which invaded these ores later, is insignificant in quantity and occurs only as intergranular space filling material.

**Martite-Magnetite-Pyrolusite-Psilomelane Ore**

This variety of ore is rather uncommon and generally composes the manganiferous iron ores which are hard and laminated. Locally, it is known as ferro-manganese ore, characterized by the presence of medium to coarse-grained martite with irregular fragments of magnetite. Interstitial spaces of these martite -
magnetite are filled with colloform pyrolusite and psilomelane. On the average this ore-assemblage contains about 30 per cent of manganese dioxide as determined by chemical analysis.

Pyrolusite-Psilomelane Ore

This manganese ore occurs scattered in irregular small pockets associated with the lateritic caprock over the hard laminated iron ores. Pyrolusite is more frequent than psilomelane. The ores are generally botryoidal indicating their colloform nature. Some crystalline pyrolusite occur either in vugs within or on the free surface of the colloform ores.

TEXTURES AND MICROSTRUCTURES

The iron and manganese ores of Bicholim and Sanquelim have several interesting and characteristic textural features. Banded structure and granular texture are very characteristic in most ores having martite and goethite as their essential constituents. In addition, colloform and replacement textures of various types are evidences of secondary ore deposits (see Schwartz, 1961). In a few cases due to preferred orientation of specular hematite, some magnetite and gangue, the ores appear schistose.

Banded Structure

The banded structure, which was the depositional feature of the protore is ideally retained by the hard and laminated iron ores consisting essentially of euhedral grains of martite
with some magnetite and massive goethite. The banding in these ores is quite conspicuous under the microscope (Plate XII, fig.1). Thin trains of goethite in some ores also serve to distinguish banding (Plate XII, fig.2). Sometimes the bands are slightly deformed. Veins of gangues or goethite occasionally cut across these bands.

Granular Texture

Granular texture is typically displayed by the ores which are largely made up of subhedral or euhedral magnetite and martite crystals with some goethite occupying the intergranular spaces (Plate XII, fig.3). When the iron ore is manganiferous, pyrolusite occurs in the interspaces of martite and magnetite, instead of goethite (Plate XII, fig.4), and in the case of protore, silica is the chief intergranular material (Plate XIII, fig.1). Generally magnetite or martite is equigranular.

The granular pyrolusite in the manganese ores exhibits mosaic texture in which the individual subhedral grains are interlocked with one another (Plate XI, fig.4).

Schistose Structure

The schistose structure is developed in a few of the hard iron ores which are composed of magnetite-martite and specular hematite with some gangue. Specular hematite shows preferred orientation of its grains (Plate XIII, fig.2). Imperfect preferred
orientation of the associated gangue minerals also occasionally serves to recognise crude schistosity. Similarly, magnetite or martite crystals also show preferred orientation of their grains (Plate XIII, fig.3).

Colloform Texture

Colloform texture was commonly observed in the lateritic manganese ores and rarely in the iron ores. The ores showing this structure are composed of a series of concentric bands of pyrolusite and psilomelane (Plate XIII, fig.4). The curvature of the bands are towards the younger free surface (see Edward, 1960, p.20). Some of the ores developed very smooth concentric bands while in others they are irregular. In a few cases there is small nucleus of ore or gangue around which concentric bands of pyrolusite and psilomelane occur (Plate XIV, fig.1). Occasionally, well-developed needles of accicular pyrolusite has a radiating pattern in the vugs (Plate XIV, fig.2). These colloform bands have also some radial shrinkage cracks. Colloform texture is, however, not common in the iron ores. The texture was only shown by the colloform variety of goethite having rare association of lepidocrocite (Plate XI, fig.2).

Replacement Texture

Replacement textures are very frequently developed in the hard laminated iron ore and less commonly, in the manganese ores. Among them pseudomorphic replacement of magnetite by martite
(Plate XIV, fig. 3), and occasionally, by goethite (Plate XIV, fig. 4) is most prevalent. The texture is of special significance since it gives direct clue to the paragenetic sequence of the ore minerals or group of minerals.

In general initial pseudomorphic replacement starts along grain boundaries (Plate XV, fig. 1), cleavage parting (Plate XV, fig. 2), fracture planes, etc. The various types of replacement textures observed in the ores are: pseudomorphic replacement, relict and vein textures.

TEXTURAL RELATIONS AND THEIR INTERPRETATION

Various textural features observed in the iron ores and some associated manganese ores furnished valuable information regarding the textural relations of the ore minerals which ultimately helped to establish their sequence of formation and processes involved therein. The iron ores are predominantly composed of hematite and goethite. Magnetite is a subordinate constituent. Lepidocrocite in these ores is still very insignificant and rare. Among the manganese minerals pyrolusite is more common than psilomelane.

The rare schistose variety is often characterised by the presence of distinctly schistose bands of flaky hematite alternating with those of granular martite. The iron minerals occupying intergranular spaces in this variety of ore is goethite. Most of the martite crystals have minute relics of magnetite which indicate incomplete chemical alteration of magnetite into martite
Specular hematite is somewhat oriented in the direction of schistosity of the ore (Plate XIII fig.2). There is no evidence to believe that martite is earlier or later than specular hematite in their relative time of appearance. The segregation of martite and specular hematite in alternate bands indicates that the two iron minerals are contemporaneous. Further, occasional presence of straight boundary relation between magnetite and specular hematite (Plate XV fig.4) is also an additional support in favour of the above view.

The hard laminated ore also consists of magnetite, martite and goethite. Careful observation often shows crude lamination in these ores. Occasionally pseudo-lamination is indicated by thin trains of goethite following laminae of the ore (Plate XII fig.2). Individual laminae of the ore is composed of martite grains which vary in size from 0.1 mm to 0.3 mm and embedded in a groundmass of goethite (Plate XIII fig.1) or gangue (Plate XII fig.3). Granular texture is characteristic of these ores. Pseudomorphic replacement of magnetite by martite was most prevalent. Initial martitization generally starts from the grain boundaries of magnetite forming an irregular rim of hematite which gradually advances inward in the form of thin lamellae following the octahedral cleavage partings of magnetite (Plate XV fig.1 and Plate XV fig.2) due to which such martites show well-developed widmanstetten like texture.

Gruner (1920a, p.378,386) has experimentally shown that a
polished surface of magnetite does not oxidize unless the surface is parallel to the octahedral plane. He advocates that for oxidation of magnetite into hematite, oxygen atom must enter into the crystal lattice of the former so that ferrous atom may convert into ferric atom.

With prolonged oxidation hematite lamellae in magnetite become wider thus decreasing the magnetite area between them. In an advanced stage of oxidation there remain only a few relics of magnetite (Plate XIV, fig.3). In certain cases the replacement is so complete that hardly any relict of magnetite is left in martite (Plate X, fig.3).

Goethite, which occurs as an intergranular space mineral, is either massive or colloform. To some extent this goethite also replaces martites (Plate XVI, fig.1). Occasionally, the colloform variety of goethite is encircled by rings of lepidocrocite showing an 'atoll' like texture (Plate XI, fig.3).

The rate of oxidation of magnetite also is not uniform as could be seen from the fact that in certain cases oxidation is more complete than in others. The rate of oxidation, however, depends upon several factors like grain size, degree of perfection of crystal lattice and the origin of magnetite. It seems in the case of smaller grains that oxidation is faster probably due to the fact that smaller grains have larger surface energy than the larger grains (see Gruner, 1926a, p.379-380; Leep, 1957, p.679). Gruner (1926a) further stated that magnetites
of sedimentary origin are more susceptible to oxidation than those of magmatic segregation and contact metamorphic origin.

A very rare case of pseudomorphic alteration of magnetite into goethite in preference to direct martite formation was noted in a few ores. Although usually relics of magnetite is absent yet the characteristic crystal shape of magnetite has been beautifully preserved (Plate XVI, fig.2). Occasionally, however, goethite is seen replacing magnetite irregularly having some relics of the latter in the former (Plate XIV, fig.4). The greater tendency of magnetite to alteration into goethite than that of hematite provides an explanation for the above fact (Girbert, 1925, p.595). Subsequently, these goethites are also replaced by martite following octahedral cleavage planes of the original magnetite, resulting wedmanstetten like texture (Plate XVI, fig.3).

Various stages of oxidation of pseudomorphic goethite into martite were recognised in these ores. At the initial stage only a few thin streaks of hematite along the margin of goethite serve to recognise the feature but with gradual advancement of oxidation an irregular rim of martite with goethite in the core is often distinct (Plate XVI, fig.4). Massive or colloform goethite, which occurs mostly within the intergranular spaces of martite, is distinguishable from pseudomorphic goethite by its lighter grey colour and distinctly red internal reflection. Moreover, in a few cases, colloform goethite also replaces the goethite pseudomorphs after magnetite (Plate XVII, fig.1).
It may be pointed out here that the pseudomorphic alteration of magnetic into goethite was commonly observed in the silica-rich iron ores or in protore.

The manganiferous iron ores, which have a common assemblage of martite, pyrolusite and psilomelane also resemble texturally the hard laminated iron ores. Larritization in these ores is generally incomplete and as a result of which martite have many irregular relics of magnetite. Colloform pyrolusite and psilomelane usually occupy intergranular spaces (Plate XVII, fig.2). These manganese minerals, in certain cases, also replace martite grains but marginally (Plate XVII, fig.3). In a few cases there are regular colloform bands of pyrolusite, psilomelane and goethite (Plate XVII, fig.4). In some other cases goethite is either veined by pyrolusite or irregular patches of goethite occur in pyrolusite indicating replacement of the former by the latter mineral.

The lateritic manganese ores have an assemblage of colloform pyrolusite and psilomelane occurring in the form of concentric or linear bands (Plate XIII, fig.4 and Plate XIV, fig.1). The prismatic and subhedral variety of pyrolusite generally occupies the vug walls and oriented perpendicular to the free surface of the colloform ores (Plate XI, fig.4). Occasionally, the crystalline variety of pyrolusite shows mosaic texture (Plate XI, fig.4).

DISCUSSION

The discussion is concerned with the following two important
topics: (1) Origin of martite and (2) martite-goethite relation.

Origin of Martite

Pseudomorphous alteration of magnetite into martite was reported from many iron ore districts of the world but frequently it was questioned as to whether the ascending hydrothermal or descending meteoric water was responsible for such an alteration. Newland (1922) was probably the first person to express doubt on the supergene origin of martite. Gruner (1930, p. 679, 837-867) has shown experimentally that magnetite oxidised to hematite in the presence of steam or water at about 258°C. This ultimately led him to conclude that martitisation was related to hydrothermal oxidation and thus considered martite to be a hypogene mineral. On the other hand Broderick (1919), Geijer (1931), Spencer and Percival (1952), Kalliokoski (1968), Teodorovich (1961) and several others cited examples of magnetite altering to hematite under supergene conditions. Therefore, according to the above mentioned workers martitization of magnetite is possible under hypogene as well as supergene conditions, though there is a greater tendency of opinion in favour of supergene origin of martite particularly, in the case of metasedimentary iron ores.

Besides the textural features, as observed under ore microscope, depth relation of the ore is another important criterion which must be taken into consideration (see Bastin 1950, p. 53). So far as the depth relation is concerned it has already been pointed out by the author that there is a gradual increase of magnetite downwards which obviously indicates that the alteration of magnetite into martite is more complete on the surface than at depth.
The martite in the present case has been considered as a supergenic iron mineral not only because of its more frequent occurrence near the surface than at depth but also on account of its intimate association with goethite of secondary origin.

Martite - Goethite Relation

Although, a considerable amount of experimental work has been done so far by Posnjak and Merwin (1922), Gruner (1930), Smith and Kidd (1949) and others to establish the relation between goethite and hematite, yet their exact natural relationship is still uncertain. Gruner (1930, p.715) on the basis of his experimental finding inferred that,

limonite is stable in the presence of water and under corresponding pressure at temperatures which approach 300°C.

But on the basis of results obtained earlier by Posnjak and Merwin (1922), Tunell and Posnjak (1931a) criticised the work of Gruner (1930). On the contrary, they (1931a) concluded that the transition temperature between goethite and hematite in a binary system \( \text{Fe}_2\text{O}_3 - \text{H}_2\text{O} \) is approximately 130°C. By another experiment they further found that goethite in a very weak HCl solution (N/10) decomposed to hematite at 100°C.

Gruner (1931, p.443), in his later experimental work, observed that goethite is unstable at 250°C, 300°C as well as at 200°C. Tunell and Posnjak (1931b, p.898), however, admitted that this observation of Gruner is nearly in accordance with their findings.
Smith and Kidd (1949) also investigated the stability relation of hematite and goethite in a neutral and alkaline solution under pressure. Their observations show that the decomposition temperature of goethite in alkaline solution is about 150° ± 20°C. They also concluded that the temperature at which goethite decomposes is insensitive to pressure as high as those found in the earth where the decomposition temperature prevails.

From the above discussion it may now be stated that decomposition temperature of goethite in acidic solution is nearly 100°C, in alkaline solution it is about 150°C and in neutral solutions nearly 130°C irrespective of the pressure. Thus, it appears that only the qualitative effect of pH may play some role in the alteration of goethite into hematite, in other words, with increasing pH dehydration temperature of goethite also increases and vice-versa.

The possibility of alteration of goethite into hematite under supergene condition was reported by Gruner, 1922; Bose, 1958; Ruckmick, 1963; and Chatterjee, 1964. But, the peculiar alteration of the pseudomorphs of goethite after magnetite into martite showing well-developed widmanstätten like texture has not yet been reported so far by any of the earlier workers.

Under the supergene condition of enrichment of iron ores it is difficult to account for a temperature of the order of 130°C required for dehydration of goethite in a neutral solution.
Therefore, the author thinks that some reaction of organic acids derived from decaying vegetation on the iron ores (see Park Jr., 1959, p.582) as well as long exposure of the near surface ore to the atmosphere might have been the cause of dehydration of goethite into hematite under supergene condition (see Ruckmick, 1963, p.231). In support of the above remark it may be stated here that all such cases of dehydration of goethite into martite are restricted to the near-surface or crustal iron ore.

PARAGENESIS

It is evident from the foregoing discussion on textural relation of iron minerals in the schistose ores that the specular hematite and those associated magnetites which show preferred orientation and straight boundary relation with specular hematite are primary minerals and hence, earliest to appear. In absence of any replacement relation between the two minerals they have been considered as contemporaneous. Among these primary minerals, magnetites have suffered extensive chemical alteration into hematites, which are included in the second generation of hematite (martite). To a limited extent magnetite has also altered pseudomorphically into goethite. From their textural relations this stage of development of goethite was deduced to be first generation and almost contemporaneous with the second generation of hematite in the time sequence. However, unlike martitization, goethitization appears to be a very uncommon process since
goethite of the first generation occurs very restrictedly. Thus, an overlapping age relation between hematite of the second generation and goethite of the first generation is envisaged. The first generation of goethite further shows evidence of pseudomorphic replacement by hematite. The age relation between two types of martite viz., one derived from magnetite and the other, from goethite, is not very clear. However, the martite associated with goethite should be later than the martite pseudomorph after magnetite if goethitization and martitization of magnetite are taken to be paragenetically overlapping or even contemporaneous. Consequently, then this later martite becomes the third generation of hematite.

The second generation of massive or colloform goethite was not only found to occur in the intergranular spaces of martite but also to replace the latter to a limited extent. Rings or bands of lepidocrocite always occur in association with colloform goethite, suggesting that both of them are contemporaneous.

Also, pyrolusite to some extent has replaced and even veined martite and goethite of later generations but in some other cases colloform bands of goethite are juxtaposed in pyrolusite and psilomelane. It is, therefore, evident that their age relation is overlapping.

The paragenetic mineral-time sequence of the iron and manganese minerals is presented in Table V.
### TABLE V

**Paragenetic sequence of the iron and associated manganese minerals of Bicholim and Sanquelim**

<table>
<thead>
<tr>
<th>Mineral sequence</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite</td>
<td></td>
</tr>
<tr>
<td>Hematite</td>
<td></td>
</tr>
<tr>
<td>Goethite</td>
<td></td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td></td>
</tr>
<tr>
<td>Pyrolusite</td>
<td></td>
</tr>
<tr>
<td>Psilomelane</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Primary</th>
<th>Supergene</th>
</tr>
</thead>
</table>

?