

## THE MINERALOGY OF ÇALDAĞ (MANİSA-TURGUTLU) LATERITIC IRON, NICKEL - COBALT DEPOSITS

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**ABSTRACT.** — The physical features, mineralogical and chemical composition of the Çaldağ Lateritic iron, nickel-cobalt deposits indicate that the ore occurs in various zones. The limonite zone, which constitutes the uppermost of the Laterite, shows iron enrichment, but high Cr and Ni levels may create some technical problems during the use of iron as an ore. The nickel content increases downwards from the limonitic zone and reaches the highest level at a zone enriched in asbolane. It decreases further downwards and shows normal values in serpentine at the bottom. As far as this study concerned, ore mineralisation in the area is smaller in size when compared to the similar deposits of the world. Nickel is commonly found in the form of silicate minerals in other lateritic deposits where as it is related to the Ni-Co-asbolane in the Çaldağ iron, nickel-cobalt deposits. The ore deposit in the area was formed as a result of the lateritic processes during the period of Upper Cretaceous - Eocene, but the lateritization did not advance and the area was covered by the Eocene formations.

### INTRODUCTION

The Çaldağ lateritic iron, nickel-cobalt deposit is located about 25 km north of Turgutlu, in the province of Manisa, Western Turkey (Fig. 1). The lateritic iron, nickel-cobalt deposit outcropping of the south of month Ayşekızı occurs in an area of 2 km<sup>2</sup>. Early studies at Çaldağ dealt with the lateritic iron formations (Brennich, 1960; Sözen, 1966; Önder, 1974; Ünlü, 1976), whereas recent research work has been concentrated on the presence of nickel-cobalt in these deposits (Yıldız, 1977; Hirano and Boyalı, 1980). The process in which the lateritization of the serpentine occurring at the bottom is thought to be responsible for the formation of iron-nickel-cobalt ore by all authors. Drilling, trenching and tunneling have been continued in the area in order to determine the reserve and grade of the ore. The studies dealing with the mineral processing have been completed at the Aegean University (Cöcen, 1980) and continued at the MTA laboratories.

Samples taken from the places favorable for Ni-Co mineralization were investigated to describe the mineralogy in detail. As a result of the mineralogical investigations on samples particularly collected by Altun, the source of high Ni-Co values was proved to be Ni-Co asbolane\*\* and not montmorillonite or garnierite as thought by other investigators (Yıldız, pers. comm.). Electron microprobe, X-ray diffraction studies and chemical analyses also supported the results obtained from microscopic studies. Following the completion of laboratory studies the authors visited the area for a period of 10 days in August 1980 to investigate the distribution of the asbolane and to clarify the mineralogy of the lateritic deposit. During these studies almost 100 representative samples were taken from the lateritic zones observed in the trenches, adits and drillcores (Fig. 1).

The field observations, microscopic investigation and chemical analyses of the samples have confirmed that the asbolane is very important for this deposit and it is the source of a considerable part of the nickel and cobalt. The aim of this work is to reveal the mineralogy of the lateritic zones of the Çaldağ lateritic iron, nickel-cobalt deposit and to help the resolution of the technological problems that may be due to insufficiently known mineralogy.

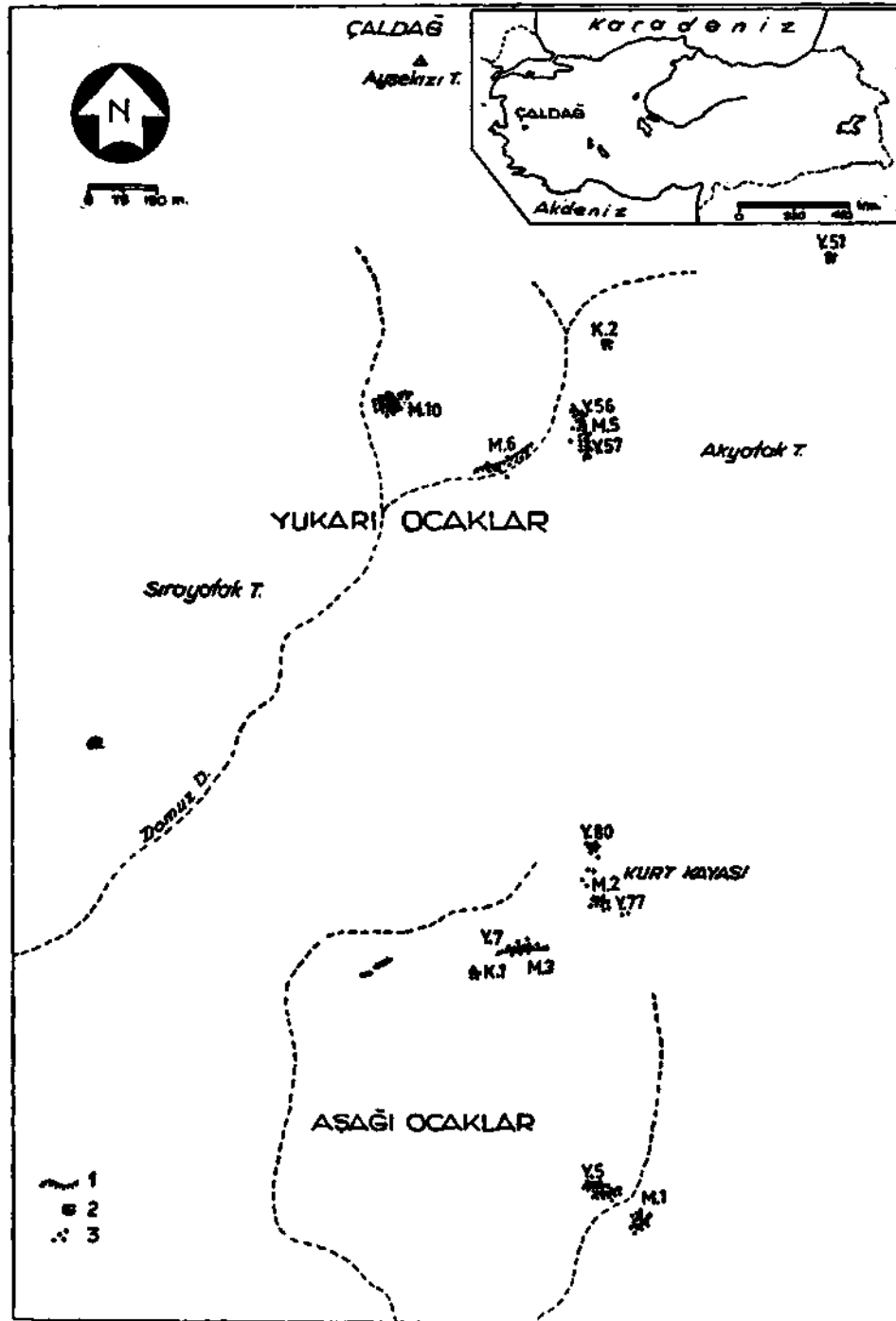


Fig. 1 - Location map and sample points.  
1 - Trench; 2 - Shaft; 3 - Sample points.

## GEOLOGY

The rocks in the Çaldağ area are Paleozoic, Mesozoic and Tertiary aged (Oğuz, 1967). Paleozoic rocks are represented by phyllite, sandstone and crystallized limestone. The grey colored crystallized limestones occurring at the bottom are represented by the white dolomite strata at the top. The ophiolitic complex formed during Upper Cretaceous shows all the units described elsewhere. The Çaldağ iron-nickel-cobalt deposit was developed on the serpentinite. The serpentinite, as a source rock (protore) of lateritisation, is surrounded by the recrystallized Paleozoic limestone on the east and south. The ophiolitic complex, including the serpentinite, extends towards the west and north-west (Oğuz, 1967). The Tertiary rocks consisting of green argillaceous strata and limestones formed in inland water conditions are partly eroded and rest on the serpentinite as isolated masses (Ozansoy, 1960; Hirano and Boyalı, 1980). These rocks are unconformable with the serpentinite and the lateritic zones. Eocene age has been given to the upper limestones by Hirano and Boyalı (1980).

The area is affected by at least two tectonic phases after the emplacement of the Cretaceous ophiolitic complex. The first phase has occurred at the beginning or before the Eocene for a short time after the lateritisation, while the second one took place after the Eocene. These features can clearly be seen around the deposit. The plasticity of the serpentinite played an important role during the tectonic deformation which caused the parting of the lateritic zones. The erosion proceeded to the unweathered serpentinite in places. The remaining laterite and serpentinite were covered by the Eocene sedimentary rocks. The tectonic activities developed after the Eocene caused dividing of the Eocene sedimentary rocks together with the serpentinite and laterite and gave these rocks dips ranging between 40-50 degrees. Later the fossil lateritic zones eroded in places again but this time the erosion was restricted because of the Tertiary cover.

The best places for the examination of the fossil laterite are the trenches from which iron has been mined (Fig. 1,2). The following lateritic zones can be distinguished. At the top a dark brown hard zone (brown limonite zone); under that a yellowish-brown, reddish-yellow, soft zone showing loose texture (yellow limonite zone); at the bottom an earthy serpentinite zone mixed with asbolane, clay minerals, calcite, limonite and chalcedony (asbolane-rich zone).

Laterite gradually changes into the unweathered serpentinite down wards. Some chert blocks and gypsum are found at the top of the laterite.

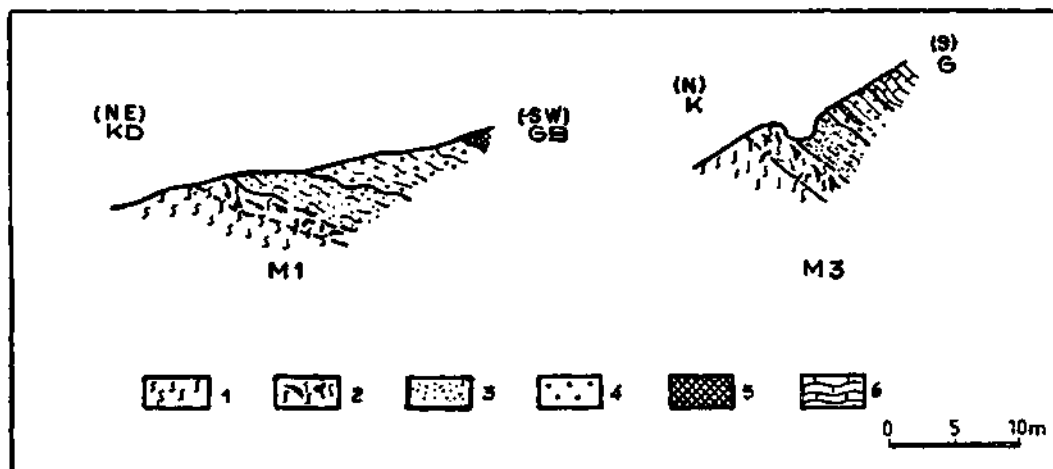


Fig. 2 - Lateritic zones observed in the M<sub>1</sub>, M<sub>3</sub> trenches.

1 - Serpentinite; 2 - Asbolane zone; 3 - Yellow limonitic zone; 4 - Brown limonitic zone; 5 - Gypsum; 6 - Limestone (Eocene).

## MINERALOGY

In this section the lateritic ore zones, enriched in iron and nickel-cobalt, the source rock (protore) serpentinite, lateritic cherts and blocks including carbonate minerals, host rocks and rare gypsum will be dealt with. The zones in the vertical section of the lateritic deposit will be described in the light of field observations and laboratory studies (Fig. 3). The ore blocks seen on the ore zone and earthy masses containing pieces of the cap rock shall not be discussed here.

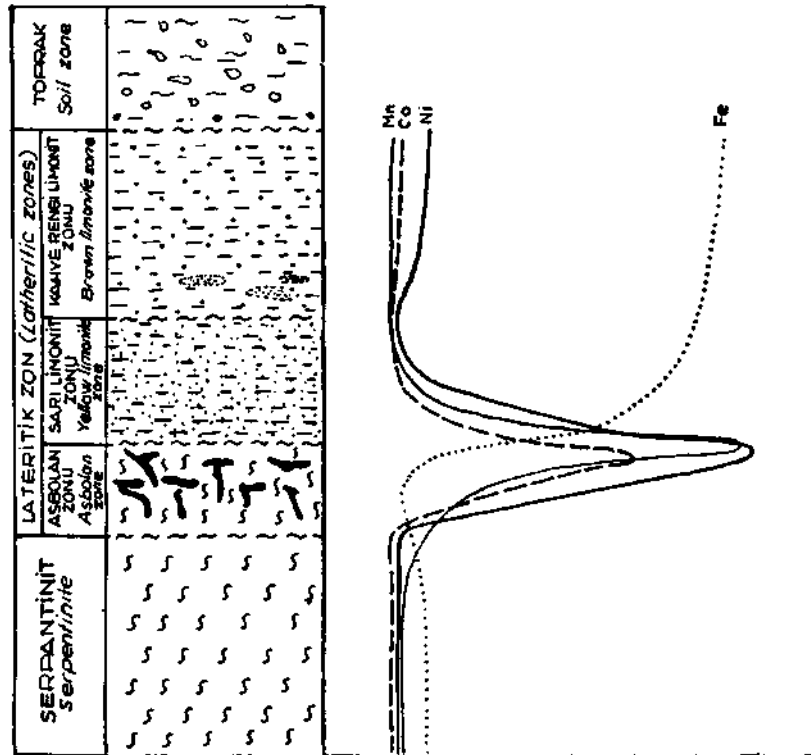


Fig. 3 - Distributions of elements in the lateritic zone.

### 1. Brown limonite zone

This is the uppermost zone of the lateritic deposit. The thickness of the zone ranges between 0,5 and 3 m. The presence of loose textured yellow limonite strata causes a partly-coloured appearance. The hardness of this zone was inherited during diagenesis as shown in the Conakry deposit (Seeliger, 1964; Percival, 1965, 1966). Beside the high proportion of the limonite, minor amounts of chromite, quartz, calcite, clay minerals and asbolane were observed in samples taken from various parts of the zone. The results of the chemical analyses of the samples collected (Kavlakoğulları et al, 1980) are given in Table 1.

*Limonite.* — Generally shows the modification of goethite and sometimes of lepidocrosite. The goetite and lepidocrosite developed as small crystals, which are closely related to each other. They show spotty surfaces. Limonite, sometimes filling the veins, forms concentric spheres and show botryoidal texture in places.

**Table 1 - Results of the analyses carried out on the brown limonitic zone**

<i>Minerals</i>									
<i>Limonite (Goethite+Lepidocrocite) found abundantly; chromite, quartz, calcite, clay minerals, asbolane occur in minor amounts</i>									
<i>Samples</i>	<i>Analysed elements (%)</i>								
	<i>Fe*</i>	<i>Cr*</i>	<i>Ni</i>	<i>Co</i>	<i>Ca</i>	<i>Mg</i>	<i>Mn</i>	<i>Si</i>	<i>Al</i>
<b>I</b>	56.64	2.10	0.7	0.03	0.4	0.2	0.15	1.0	0.4
<b>II</b>	56.02	1.61	0.7	0.02	0.7	0.2	0.15	2.0	1.0
<b>III</b>	54.72	1.84	0.1	0.007	1.5	0.3	0.15	0.7	0.4
<b>IV</b>	53.22	2.61	0.6	0.02	0.6	0.2	0.2	1.0	1.5
<b>V</b>	51.44	2.79	0.7	0.04	1.0	0.3	0.15	1.5	2.0
<b>VI</b>	50.44	2.81	0.7	0.04	1.5	0.4	0.15	2.0	2.0
<b>Average</b>	<b>53.74</b>	<b>2.29</b>	<b>0.6</b>	<b>0.03</b>	<b>1.0</b>	<b>0.3</b>	<b>0.16</b>	<b>1.4</b>	<b>1.2</b>

Those analyses marked with\* are quantitative, others representing semi-quantitative optical spectrographic analyses.

*Chromite.* — It is pale-coloured (brownish-tinge) compared to ordinary chromite. The chromite crystals are usually euhedral and exhibit cataclastic texture. Their size varies from 10-15 micron up to 1-1,5 mm. The dimension of the crystals increases downwards in this zone. The chromite is also seen in the fractures and cavities as fine grains (chromite dust). The mineralogic investigations of these fine grains revealed that the chromite crystals are dark gray or brown tinted, euhedral and subhedral, and cataclastic. In the same samples minor goethite and trace hematite are also observed. The largest crystal in the chromite dust is 1 mm. Some traces of the serpentinite are found in the cataclastic fractures. The chemical analyses of this sample gave 31.23 % Cr. These evidences suggest that the chromite was mobilised during the lateritic alteration zone as a heavy fine-grained mineral. A similar behaviour of the chromite during lateritic alteration was described by Seeliger (1964) in the Conakry lateritic iron deposit (West Africa).

*Quartz.* — Minor amounts of small quartz crystals are present in the limonite. Quartz is occasionally found in the veinlets and pods.

*Calcite and clay minerals.* — These minerals are generally observed as veinlets, filling the fractures and cavities.

*Asbolane.* — Mostly occurring in the veinlets and pods is seen with the goethite as interlocking crystals. Very fine-grained asbolane shows a variety of colours.

## 2. Yellow limonite zone

Underlies the brown limonite zone and is porous, soft and sometimes earthy; thin limonite layers occurring in the lower part of the brown limonite zone also show similar features. The thickness of the yellow limonite zone varies, reaching up to 2-2,5 m in the iron rich trenches. The microscopic examination of the samples collected from this zone revealed a high proportion of goethite, minor chromite, clay minerals and quartz. The chemical composition of these samples are given in Table 2.

*Goethite.* — Is very fine grained and gives a coloured appearance to the sample. Although its proportion varies from sample to sample, goethite is the main mineral of this zone.

**Table 2 - Results of the analyses carried on samples taken from the yellow limonitic zone**

<i>Minerals</i>									
<i>Goethite found abundantly; clay minerals, carbonates, quartz found less than goethite; chromite and asbolane occur in minor amounts</i>									
<i>Samples</i>	<i>Analysed elements (%)</i>								
	<i>Fe*</i>	<i>Cr*</i>	<i>Ni</i>	<i>Co</i>	<i>Ca</i>	<i>Mg</i>	<i>Mn</i>	<i>Si</i>	<i>Al</i>
<b>I</b>	51.10	1.75	0.2	0.015	0.15	0.2	0.1	2.1	1.5
<b>II</b>	49.60	1.8	0.4	0.02	0.3	0.4	0.3	2.7	2.3
<b>III</b>	43.80	2.15	0.8*	0.02	0.2	0.3	0.2	3.4	2.5
<b>IV</b>	39.45	1.9	2.2*	0.04	0.6	0.7	1.6	5.7	4.8
<b>V</b>	34.60	1.61	2.56	0.15	0.7	0.3	2.5	7.0	4.0
<b>Average</b>	<b>43.71</b>	<b>1.8</b>	<b>1.23</b>	<b>0.02</b>	<b>0.4</b>	<b>0.4</b>	<b>0.9</b>	<b>4.1</b>	<b>3.01</b>

These analyses marked with\* are quantitative, others representing semi-quantitative optical spectrographic analyses.

*Chromite.* — Occurs as euhedral and cataclastic crystals varying up to 1-1,5 mm in size. The brownish chromite seen in the brown limonite zone and dark grayish chromite observed in the serpentinite occur in the yellow limonite zone. The cataclastic fractures in the chromite are filled by goethite. The chromite in the lateritic zone displays a sorting effect with the coarsest grains at the base and the finest grains at the top.

*Quartz/carbonate and clay minerals.* — These minerals occur in minor amounts, usually filling fractures and cavities. Their proportion increases downwards in the zone. Because they are stained by goethite, it is difficult to recognize these minerals in thin sections. But the macroscopic or microscopic identification of montmorillonite and halloysite which are observed at the lower levels of the zone is relatively easy because of their distinct green and bluish colour.

*Asbolane.* — Asbolane is enriched at the lower levels of the zone particularly relating to the content of the clay minerals. The Manganese-rich zones and nickel-cobalt-rich zones in the asbolane were crystalized together side by side and inside each other and occasionally fill the fractures and cavities. They form small concentric crusted spheres and show kidney-like and botryoidal textures. This mineral will be further described under the section «Asbolane-rich zone».

### 3. Asbolane rich zone

Varies in thickness and is located between the unweathered serpentinite and yellow limonite zone in an unspoiled section of the lateritic zone. 1-2 m upper part of this zone is enriched in nickel-cobalt. The mineral type causes the colour varieties of yellowish green, deep blue, brown and black. In the samples taken from this zone the following minerals, beside the serpentine were observed: locally enriched asbolane, clay minerals (montmorillonite, nontronite, halloysite), chalcedony (partly green chrysoprase), calcite, chlorite, limonite, chromite, magnetite and hematite. Some selected samples from this nickel-cobalt-rich zone were analyzed and the results are given in Table 3.

*Serpentine.* — The serpentinization of the olivine and orthorhombic pyroxene in the peridotite produced the serpentinite. The network crystalization of the antigorite after olivine is commonly, and the bastite as pseudomorphs of the pyroxene are occasionally, seen in the samples.

Table 3 - The results of the analyses of asbolane rich zone

Samples	Minerals												
	Mainly asbolane, clay minerals, calcite, chalcidony and serpentine rich samples; limonite, chromite, martitized magnetite occur in minor amounts											K <sub>2</sub> O*	
	Ni*	Co*	Fe	Mn	Ca	Mg	Cr	Al	Si	Zn	As		
Analysed elements (%)													
I	4.55	0.07	7.0	~ 3.0	~ 4.0	~ 4.0	~ 4.0	0.15	> 10.0	> 10.0	G	G	0.04
II	3.02	0.3	4.0	~ 4.0	1.5	~ 4.0	~ 4.0	0.3	> 10.0	> 10.0	G	G	0.04
III	15.08	0.2	10.0	~ 6.0	2.0	0.4	1.3	~ 10.0	> 7.0	> 7.0	G	G	0.05
IV	6.18	0.2	4.0	~ 3.0	~ 10.0	~ 2.0	0.4	> 10.0	> 10.0	> 10.0	G	G	0.04
V	5.05	0.4	7.0	~ 5.0	~ 2.0	3.0	0.7	> 10.0	> 10.0	> 10.0	0.2	G	0.05
VI	0.3	0.01	1.5	0.03	~ 10	0.7	0.7	4.0	2.0	2.0	G	G	0.02
VII	3.99	0.15	4.0	~ 2.0	0.7	1.5	0.3	~ 2.0	> 10.0	> 10.0	0.15	G	0.04
VIII	1.85	0.3	3.0	~ 1.5	0.7	~ 0.6	1.65	> 10.0	51.04	G	G	G	0.03
IX	0.7	0.04	3.0	0.8	~ 10	1.5	0.4	~ 10.0	~ 10.0	~ 10.0	G	G	0.02
X	2.40	0.2	3.0	~ 2.0	~ 1.0	~ 4.0	0.3	4	> 10.0	> 10.0	G	G	0.03
XI	2.70	0.15	4.0	2.0	0.7	~ 1.5	0.71	~ 10.0	> 10.0	> 10.0	G	G	0.04
XII	1.42	0.15	3.0	1.0	~ 10.0	0.3	0.15	1.5	> 10.0	> 10.0	G	G	0.03
Average	3.93	0.18	~ 5	~ 4	~ 7	~ 3	0.6	> 10	> 10.0	> 10.0	0.002	G	0.04

Those analyses marked with\* are quantitative, others representing semi-quantitative optical spectrographic analyses.

*Asbolane.* — Asbolane can easily be recognized by its black colour. It is found with the clay minerals and generally occurs in the upper levels of the zone and in the fractures and cavities of the serpentinite (Plate I, fig. 1). Although the thickness of the asbolane veins varies, it's 15-20 micron in the fractures and cleavages of the serpentine (Plate I, fig. 2) and of the bastites (Plate I, fig. 3) and sometimes rises to 0,5-1 cm in the serpentinite. Fine veinlets finger into the serpentinite from the wide veins. The asbolane in the wider fractures, and cavities occasionally developed in the well-formed concentric shells and kidney-like structures which can even be seen by the naked eye.

The asbolane is observed in the microscope as two slightly different aggregates showing gray-dark gray color and gray with pinkish-brown tinges. However the colours of the aggregates sometimes gradually change into each other. Each aggregate is formed by submicroscopic grain boundaries which can not be distinguished under the microscope. Largest grains of the asbolane which developed as concentric shells (Plate I, fig. 4,5,6), showing kidney-like, botryoidal textures (Plate I, fig. 7,8) and sometimes radiating crystals (Plate II, fig. 1,2,3) are found in the central parts of the veins and concentric spheres (Plate II, fig. 4), as well as between the concentric shells. Size of the grains usually forming needlelike crystals are as much as 1,5-20 micron in length and 3-5 micron in width (Plate II, fig. 1). These grains are strongly pleochroic and anisotropic. The pleochroism and anisotropy are poor in the submicroscopic crystallized parts of the asbolane showing spotty surfaces (Plate II, fig. 2). The ratios of microscopically determined asbolane varieties (Plate I, fig. 4) are different in the asbolane veins. The asbolane usually occurring with clay minerals and sometimes with limonite, forms concentric shells as it is stated above. Clay minerals also developed as concentric shells with the asbolane (Plate II, fig. 5,6). The pinkish-brown tinged asbolane occasionally replaces the idiomorphic minerals and occurs inside the idiomorphic-subidiomorphic, partly martitized magnetite.

The X-ray diffraction studies on some samples taken from the asbolane veins have revealed that the asbolane is amorphous. The minerals of heubachite  $((\text{Ni}, \text{Co}, \text{Fe})_3\text{O}_4 \cdot 6\text{H}_2\text{O})$  (Dana and Dana, 1944) and heterogenite  $(\text{CoO} \cdot \text{Co}_2\text{O}_3 \cdot 6\text{H}_2\text{O})$  (Ramdohr, 1975) were not identified in the nickel-cobalt-rich part of the asbolane. The quantitative analyses have not revealed important proportions of Ni, Co, Mn and Fe (Table 4).

**Table 4 - The analyses of the asbolane rich samples**

<i>Samples</i>	<i>Analysed elements (%)</i>			
	<i>Ni</i>	<i>Co</i>	<i>Mn</i>	<i>Fe</i>
<b>I</b>	<b>8.60</b>	<b>0.95</b>	<b>12.46</b>	<b>3.58</b>
<b>II</b>	<b>7.85</b>	<b>0.32</b>	<b>15.37</b>	<b>2.13</b>
<b>III</b>	<b>6.22</b>	<b>1.23</b>	<b>14.18</b>	<b>3.63</b>
<b>IV</b>	<b>5.73</b>	<b>1.05</b>	<b>13.17</b>	<b>4.25</b>

13 electron probe microanalyses have been done on the concentric crusted asbolane in the laboratories of Cambridge University by Dr. J. Rossol. In addition, 2 electron probe microanalyses have been completed on the asbolane vein, in the MTA laboratories (Öztuğ, 1981). These analyses are given in Table 5. The topographic picture and MnK, NiK, FeK, CoK appearances of the microprobed asbolane vein are shown in Plate II, fig. 7,8 and Plate III, fig. 1,2,3.

Total element oxides, as it is seen in the table, vary between 60-75 %. The rest is attributed to the free-water in the asbolane. The values of MgO, CaO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> are thought to be derived from the inclusions in the amorphous asbolane.



Table 5 - The results of the microprobe analyses of pinkish brown-gray asbolane

Element oxides	Concentric asbolane													Asbolane vein	
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII		
NiO	22.314	21.550	18.919	18.797	20.398	17.115	17.720	15.911	19.975	18.604	17.325	16.470	15.108	10.931	11.444
CoO	—	—	—	—	—	—	—	—	—	—	—	—	—	11.025	8.050
MnO	34.628	32.210	31.519	32.041	35.952	28.933	28.933	28.962	34.716	30.928	32.548	36.897	37.949	39.500	26.270
FeO	0.544	0.410	0.789	0.528	0.447	0.386	0.386	0.474	0.816	0.429	0.437	0.490	0.433	1.166	1.830
MgO	0.348	0.313	0.311	0.268	0.286	0.504	0.633	0.274	0.255	0.282	0.284	0.748	0.614	1.850	1.005
CaO	0.722	0.648	1.006	1.094	0.842	1.474	1.451	1.595	0.555	0.840	0.675	1.710	2.028	0.916	0.653
Al <sub>2</sub> O <sub>3</sub>	9.235	12.642	10.411	8.696	7.989	12.638	10.230	5.943	11.132	5.249	12.238	6.396	6.952	4.506	13.491
Cr <sub>2</sub> O <sub>3</sub>	1.059	1.032	0.699	0.966	1.589	0.454	0.487	0.533	1.130	0.632	0.606	0.195	0.309	0.510	0.220
SiO <sub>2</sub>	6.181	7.538	9.841	8.337	4.219	13.446	11.064	3.166	4.899	4.403	5.333	3.094	2.122	1.716	14.743
Total	75.029	76.452	73.496	70.228	71.723	75.057	71.000	62.774	71.547	61.367	69.455	66.001	65.515	72.120	77.706

*Clay minerals.* — Occur in shades of green and indigo blue. They are observed under the microscope as homogenous, colloidal textured (Plate III, fig. 4), and sometimes fibrous minerals in the fissures, fractures, cavities and meshworks of the serpentinite. The clay minerals which occur in various shades of yellowish, greenish, dark green, pink and purple are occasionally coloured to brown-red by limonite. X-ray diffraction, D.T.A., and refractive indice oils and optical mineralogy studies on the clay minerals have revealed that the pale coloured minerals are of montmorillonite-beidellite group and green-purple coloured ones of nontronite group. Large crystals of nontronite which in places constitute 20-30 % of the clay minerals show a distinct pleochroism. The indigo-blue clay minerals are identified as montmorillonite-halloysite by D.T.A. studies. The semiquantitative optical spectrographic analyses of the clay mineral-rich samples sometimes including little amount of asbolane, chromite, martitized magnetite and limonite are shown in Table 6.

**Table 6 - The semiquantitative optical spectrographic analyses of the clay mineral rich samples**

<i>Clay minerals found abundantly; chromite, magnetite, limonite, asbolane occur in minor amounts</i>													
<i>Samples</i>	<i>Analysed elements (%)</i>												
	<i>Ni</i>	<i>Co</i>	<i>Fe</i>	<i>Mn</i>	<i>Ca</i>	<i>Mg</i>	<i>Cr</i>	<i>Al</i>	<i>Si</i>	<i>Zn</i>	<i>As</i>	<i>Cu</i>	<i>K<sub>2</sub>O</i>
<b>I</b>	0.4	0.02	1.5	0.7	0.15	0.2	8.75*	10	10	G	G	0.0015	0.04
<b>II</b>	0.2	0.015	3.5	0.3	0.80	0.4	0.55	10	10	G	G	G	0.03
<b>III</b>	0.3	0.01	2.15	0.55	0.35	0.3	0.74	10	10	G	G	G	0.04
<b>IV</b>	0.2	0.035	1.65	0.34	0.15	0.5	0.65	10	10	G <sub>1</sub>	G	G	0.05
<b>Average</b>	<b>0.28</b>	<b>0.02</b>	<b>2.20</b>	<b>0.47</b>	<b>0.36</b>	<b>0.35</b>	<b>2.67</b>	<b>10</b>	<b>10</b>	<b>G</b>	<b>G</b>	<b>G</b>	<b>0.04</b>

Those analyses marked with\* are quantitative, others representing semi-quantitative optical spectrographic analyses.

The clay minerals, as seen in the Table 6, are very poor in nickel and cobalt. Nickel content is assumed to be partly derived from asbolane found in the clay minerals.

*Chalcedony-Quartz.* — Are usually in grass-green and yellowish green (chrysoprase). Chalcedony is observed as spheroids in thin sections (Plate III, fig. 5). Clay and chlorite minerals fill the open spaces between the spheroids. Calcite veins are present in some samples. Chalcedony is coloured by limonite in places. Cataclastic chromite grains sizing up to 1 mm and placed in particular lines rarely occur in the chalcedony. Quartz is developed as coarser grains. The analyses of the chrysoprase and mixture of chalcedony+clay minerals are given in Table 7.

**Table 7 - The analyses of the chrysoprase and mixture of chalcedony+clay minerals**

<i>Minerals</i>													
<i>I. Chrysoprase; chlorite, clay minerals, chromite occur in minor amounts; trace limonite, asbolane</i>													
<i>II. Chalcedony, clay minerals; chromite occur in minor amounts; trace limonite, asbolane</i>													
<i>Samples</i>	<i>Analysed elements (%)</i>												
	<i>Ni</i>	<i>Co</i>	<i>Fe</i>	<i>Mn</i>	<i>Ca</i>	<i>Mg</i>	<i>Cr*</i>	<i>Al</i>	<i>Si*</i>	<i>Zn</i>	<i>As</i>	<i>Cu</i>	<i>K<sub>2</sub>O</i>
<b>I</b>	0.3	0.02	4.0	0.07	0.03	0.4	2.07	1.0	84.84	G	G	0.003	0.04
<b>II</b>	0.2	0.007	3.0	0.03	0.2	0.5	6.15	10	45.98	G	G	0.01	0.04

Those analyses marked with \* are quantitative, others representing semi-quantitative optical spectrographic analyses.

*Calcite.* — Anhedral and subhedral crystals of calcite occur in the fractures and cavities of the serpentinite with various proportions of chalcedony, clay minerals, limonite, asbolane, martitized magnetite and chromite. Beside the calcite veinlets which are sometimes coloured by limonite a number of magnesite veinlets are also present.

*Chlorite.* — Found together with chalcedony and the clay minerals and may constitute up to 3-4 % of the bulk. It is heterogeneously distributed along the fractures and cracks of the clay minerals and shows dark green-pale green pleochroism. The angle between optic axes is  $2V(-)=O$ . This phyllosilicate is probably Ni-chlorite.

*Limonite.* — Occurs with asbolane, clay minerals, calcite, chromite and magnetite in the fractures and cavities of the serpentinite. The limonite colouring silicates is usually goethite. It occasionally shows colloidal texture.

*Chromite.* — Is very rare in this zone. It is generally euhedral, subhedral and cataclastic with sizes up to 1-1,5 mm. Chromite in this zone resembles in many ways to that in the fresh serpentinite. It is sometimes replaced by magnetite along the fractures and mineral boundaries. Chromite is enriched in asbolane, clay minerals, calcite and limonite rich veinlets which cut the serpentinite.

*Magnetite.* — Crystallised very little in two forms: One is in the pseudomorph forms of euhedral and subhedral chromite and other is in the forms of some veinlets and little, anhedral grains resulting from serpentinization. Partial magnetization of the chromite developed during the serpentinization. Chromite relicts are present in this kind of magnetite. Magnetite veins are observed in and between the olivine pseudomorphs, pyroxene pseudomorphs and in the cleavages and fractures of bastites. The magnetite grains and veins are partly replaced by magnetite and hematite along grain boundaries or cleavages. The magnetite, like the chromite, together with the clay minerals and asbolane is enriched in the fractures of the serpentinite to certain extent.

*Hematite.* — Generally developed as a result of partial or complete martitization of the magnetite and is present in minor amounts.

*Heazlewoodite-arparuite.* — Occasionally and very little found in this zone as grains sizing up to 30-40 microns (Plate III, fig. 6).

#### Fresh serpentinite

Being the source rock of the lateritization underlies the asbolane-rich zone. Some magnesite veins and small chromite bodies occur in the rock.

The fresh serpentinite includes meshwork textured antigorite and bastites with pseudomorph of orthopyroxene, and was produced by the serpentinization of the peridotite (harzburgite, dunite). In the polished sections of the serpentinite the following minerals are observed: partly martitized small magnetite grains sizing up to 1,5 mm and occasionally oriented in particular directions and up to 30-40 micron sized heazlewoodite (Plate III, fig. 7) and awaruite (Plate III, fig. 8). The chromites are sometimes replaced by magnetite and chrome-spinel along boundaries of the grains and cataclastic fractures. The chemical analyses of the serpentinite samples gave the values in the range 0,19-0,22 % Ni, 0,013-0,016 % Co and 0,3-0,4 % Cr.

#### Other rocks around the ore deposit

*Paleozoic Dolomitic limestone.* — Usually surrounds the serpentinite and occasionally occurs in the serpentinite as blocks. It consists of subhedral and euhedral carbonate crystals. Secondary calcite

veins containing minor limonite-asbolane developed between the carbonate crystals and in the fractures, in the samples taken from the area near the serpentinite boundary and from the blocks in the serpentinite.

*Chert blocks.* — Generally overlie the limestone which covers the laterite zone and are sometimes found over the serpentinite. These blocks formed as a result of accumulation of silica in suitable environments during lateritization and were broken and moved away by late tectonic activities. Quartz and chalcedony are the main constituents while carbonate minerals (calcite) occur in the fractures and cavities. Minor amounts of brown tinged chromite, limonite as veinlets and plain material, trace pyrite and marcasite are found in the blocks, cataclastic chromites size up to 1 mm. A sample showing above features has been determined to contain 0,1 % Ni, 0,007 % Co, 0,3 % Mn and 7 % Fe.

*Cherty Limestone covering lateritic zone.* — Can be best observed in the M<sub>3</sub> trench (Fig. 2). Minor amounts of opal-chalcedony and quartz fill the spaces between the subhedral and euhedral calcite crystals. Dark gray chromite, limonite, marcasite + pyrite, magnetite and trace, asbolane are found in the samples. The biggest chromite grain is 1 mm. Limonite occurs as pseudomorphs of an euhedral mineral or vein material. The pyrite-marcasite aggregates, in places, are replaced by the limonite along grain boundaries. The asbolane is found in the limonite veins. The chemical analyses of this rock shows 0,3 % Ni, 0,02 % Co, 0,4 % Mn, 0,4 % Cr, 7 % Fe, 5 % Si, 0,4 % Al and 0,3 % Mg.

*Gypsum rock.* — Is very little and locally observed in the M1 trench as euhedral, subhedral crystals. The rock contains minor chromite, serpentine, marcasite, goethite, pyrite, quartz, calcite, clay minerals and asbolane. The sizes of the cataclastic chrome grains are between 15-20 micron and 1,2 mm. The marcasite grains being usually anhedral with sizes from 10-15 micron to 400 micron. The pyrite is found in the central parts of some marcasite grains. The chemical analysis of the gypsum rock gives 10 % Fe, 2,47 % Cr, 0,15 % Ni, 0,015 % Co and 0,2 % Si.

*Eocene Limestone.* — Showing structural features like stromatolites and containing organic material consists of micrite and smaller proportions of microsparite.

## DISCUSSION OF THE LATERITIC FORMATION

As it is generally known some Ni and Co occur in the crystal lattice of olivine and orthopyroxene. Ni is masked by Mg in olivine and pyroxene (Cameron, 1971). The serpentinitization does not change the Ni content of the original rock, the peridotite, but during this process, nickel occurring as diadochic substitution in the olivine and pyroxene forms Ni-sulphides. Heazlewoodite (Ni<sub>3</sub>S<sub>2</sub>) and awaruite (Fe-Ni alloy) were formed as a result of serpentinitization in Çaldağ. The nickel-bearing minerals produced by the serpentinitization of peridotite have been studied by many authors (Nickel, 1959; Heekli, 1963; Ramdohr, 1967; Eckstrand, 1970; Rucklidge, 1971; Walde, 1971; Guillen-Lawrence, 1973; Dick, 1974; Groves et al., 1974; Eckstrand, 1975; Çağatay, 1975a and 1975b; Helke and Çağatay, 1978).

The peridotites and fresh serpentinites contain approximately 0,3 % Ni and 0,02 % Co according to Goldschmidt (1954); 0,2 % Ni and 0,015 % Co according to Turekian and Wedepohl (1961); 0,2 % Ni and 0,02 % Co according to Vinogradov (1962); and 0,15 % Ni, 0,011 % Co, 0,104 % Mn and 0,003 % Cu according to Goles (1967). Gülaçar has determined 0,2 % Ni and 0,01 % Co in the ultrabasic rocks taken from various parts of Turkey. The results of Vhay (1973) are also similar. The nickel and cobalt values of the Çaldağ fresh serpentinite are 0,19-0,22 % and 0,013-0,016 % respectively, which agrees well with the other results.

After the serpentinization the tropical-Subtropical climate during Upper Cretaceous-Eocene caused lateritization in the Çaldağ area. Smirnov (1976) has revealed that Mg liberated during the alteration of serpentinite was carried away as easily solvable salts, some of which, together with the clay minerals, formed magnesite veins. The liberated Si moved as  $\text{SiO}_2$  solutions, accumulated in morphologically suitable hollows and formed cherts or descended in the lateritic zone and crystallized chalcedony and quartz veins. Al produced by lateritization, moved in vertical direction and formed the clay minerals, such as montmorillonite, beidellite, nontronite and halloysite, in the asbolane-rich zone. The magnetite in the serpentinite was first martitized and replaced by the hematite and later the limonite (generally goethite) developed which produced limonite zones in the laterite. The gray chromite in the serpentinite was the least affected by the lateritization. This gives a brownish appearance to the limonite. The chromite is enriched in the limonite zone in proportion to the iron. The chromite grains filled the fractures and cavities of the limonite zone, particularly of the brown limonite zone and show distinct grading and orientation in certain directions. Similar features of chromite have been reported by Seeliger (1964) in the Conakry lateritic iron deposit (West Africa). The heazlewoodite and awaruite observed in the serpentinite were formed during the lateritization. Nickel and cobalt solutions carrying manganese moved downward precipitating the asbolane and the clay minerals in the fractures and cavities of the lower parts of the limonite zone.

It is interesting that a large proportion of nickel in the Çaldağ lateritic iron nickel-cobalt deposit is associated with asbolane whereas the nickel in other lateritic nickel deposits usually belong to the silicates e.g. nickel-chrysotile (garnierite), nickel-saponite (pimelite), nickel-talk, nickel-chlorite (Shuardite) (Faust, 1966; Perruchot, 1971; Springer, 1974) and nickel-nontronite (Magakyan, 1968). Nickel in the deposits with complete lateritization is generally enriched in the lower parts of the cobalt-rich asbolane zone as nickel-silicates. The occurrence of nickel together with cobalt, in the asbolane in Çaldağ and not as nickel-silicates in the lower parts indicate that the Çaldağ deposit has not completed the lateritization process.

The Eocene limestones covering the Çaldağ lateritic iron, nickel-cobalt deposit and the Paleozoic limestones surrounding the deposit are the source of some calcium in the lateritic zone. The Ca solutions derived during the deposition of younger limestones and dissolved from two limestones moved downwards in the lateritic zone and formed secondary calcite veins. The high Ca content of the lateritic zone has partly originated from these calcite veins and partly from the clay minerals.

The gypsum observed in little amounts in the deposit occurs as Eocene evaporite formations in various parts of Turkey (Uygun, 1980).

## CONCLUSION

1. The Çaldağ iron, nickel-cobalt deposit is small, as far as it is known, and did not complete its lateritization process.
2. The economic nickel mineral in the deposit is asbolane.
3. The chemical analyses of the samples consisting of clay minerals and containing very little asbolane show very low values of nickel-cobalt. Some of the nickel present in the ore is thought to be related to the nickel-silicates.
4. Using the limonitic zone in the upper levels of the lateritic zone as iron ore is thought to be unsuitable because of the nickel content and unwanted chrome values.

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# PLATES

#### PLATE - I

- Fig. 1 - Magnification X 200, thin section. Intergrowths of the asbolane vein (black) with clay minerals (gray) in serpentine.
- Fig. 2 - Magnification x 300, in oil, polished section. Asbolane veins (white) in the cracks of serpentine.
- Fig. 3 - Magnification X 300, in oil, polished section. Asbolane (white) in the cleavages of bastite.
- Fig. 4 - Magnification X 300, in oil, polished section. Asbolane and clay minerals form spheres with concentric crusts (white-pale gray).
- Fig. 5 - Magnification x300, in oil, polished section. Intergrowths (concentric crusted and reniform) of the asbolane (white-pale gray) with clay minerals (gray-dark gray).
- Fig. 6 - Magnification X 300, in oil, polished section. Intergrowths (concentric crusted) of the asbolane (two different coloured, white-gray) with clay minerals.
- Fig. 7 - Magnification X 300, in oil, polished section. Fine grained and reniform asbolane (at the centre). The kidney shaped parts show different colours because of the high reflection pleochroism of the asbolane.
- Fig. 8 - Magnification X 300, in oil, polished section. Matted surfaced asbolane in the concentric crusted asbolane (white). Gang=clay minerals (dark coloured).

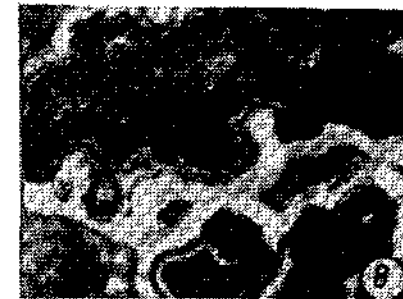
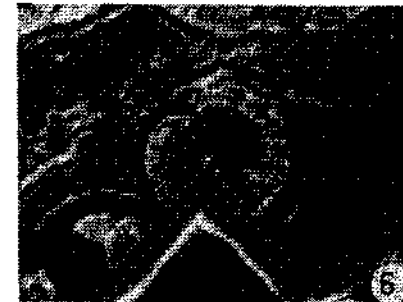
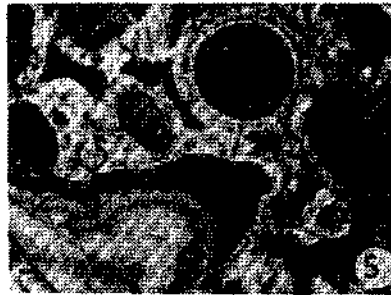
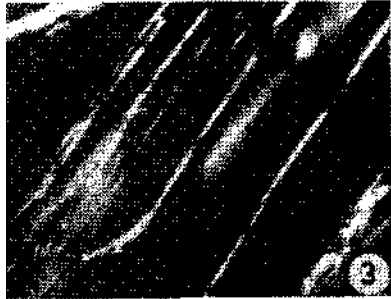


PLATE - II

- Fig. 1 - Magnification x 300, in oil, polished section. Concentric crusted, radial and matted surfaced asbolane. Needles show different colours because of the reflection pleochroism.
- Fig. 2 - Magnification X 300, in oil, polished section. Radial asbolane (show high reflection pleochroism).
- Fig. 3 - Magnification x 300, in oil, polished section. Radial asbolane (white) in clay minerals.
- Fig. 4 - Magnification x 300, in oil, polished section. Fine grained asbolane aggregates (pale gray). At the centre different coloured (because of the high reflection pleochroism), coarse grained asbolane.
- Fig. 5 - Magnification X 300, in oil, polished section. Concentric crusted asbolane (white) in the clay occurrences (Dark gray).
- Fig. 6 - Magnification X 300, in oil, polished section. Asbolane (white) and clay minerals form intergrowth with crusted shapes.
- Fig. 7 - Magnification x 500, polished section. Back scattered electron image of asbolane (fibrous). Gang serpentine (dark gray).
- Fig. 8 - Magnification x 500, polished section. Mn Ka image of asbolane.

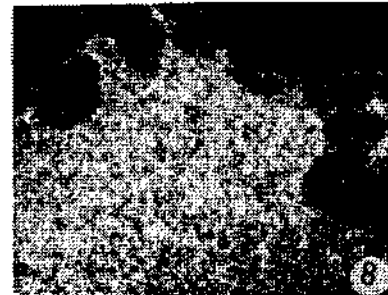
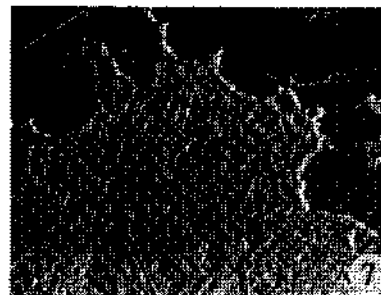
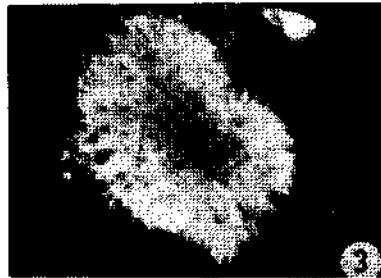
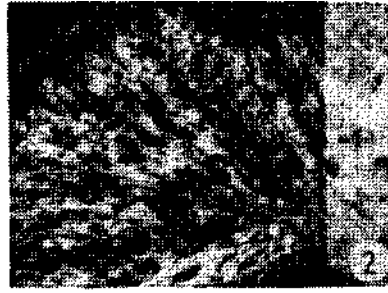
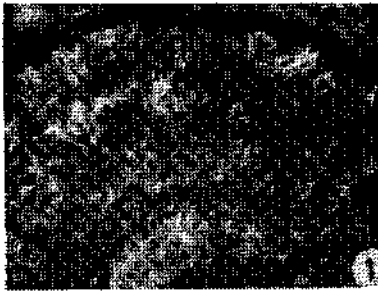


PLATE - HI

Fig. 1 - Magnification X 500, polished section. NiKa image of asbolane.

Fig. 2 - Magnification X 500, polished section. FeKa image of asbolane.

Fig. 3 - CoKa image of asbolane.

Fig. 4 - Magnification X 300, in oil, polished section. Asbolane (white) in concentric crusted clay minerals.

Fig. 5 - Magnification X 200, thin section. Small spherulitic chalcedonies. Clay minerals (black).

Fig. 6 - Magnification x 300, in oil, polished section. Awaruite (at the centre, white) in clay minerals. Asbolane veins with matted surface.

Fig. 7 - Magnification X 300, in oil, polished section. Heazlewoodite (white, at the centre) in serpentine (gray).

Fig. 8 - Magnification X 300, in oil, polished section. Heazlewoodite (white, at the centre) in serpentine (gray).

