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MINERALOGICAL AND GEOCHEMICAL CHARACTERISTICS OF THE BENAVI IRONSTONE DEPOSIT, NORTHERN IRAQ

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ABSTRACT

The Benavi ironstone deposit is a stratiform iron mineralization within the Jurassic – Cretaceous sequence of the Imbricate Zone (N Iraq). It is composed of several mineral assemblages including iron oxides/ hydroxides (hematite, goethite, limonite and magnetite), sulfides (pyrite and arsenopyrite), carbonates (calcite, siderite and ankerite), silicates (kaolinite, chamosite, and glauconite), quartz and apatite. The main iron minerals are hematite and goethite. Goethite formed as a result of oxidation processes of pyrite, siderite and chamosite under surface weathering. Calcite is the main non-iron mineral in the Benavi ironstones, mostly containing Mg^{+2} and Fe^{+2}, while siderite and ankerite are minor. Kaolinite and chamosite are the main clay minerals in the ironstone whereas glauconite is trace. Arsenopyrite is found restricted at the base of the Benavi ironstone outcrop, having dark grey color in the field, associated with chamosite, pyrite, apatite and glauconite. Chemical analyses showed that Fe_2O_3 ranges between 3.28 – 33.9 wt.% with an average of 20.44 wt.%, which is considered as a low-grade ironstone deposit. Replacement of calcareous components by iron minerals is indicated by the very strong negative correlation between CaO and Fe_2O_3, suggesting epigenetic ore formation by the diagenetic replacements of carbonate rocks. The significant role of diagenetic processes is supported by the negative correlation of CaO with SiO_2, Al_2O_3, P_2O_5, Co, Ni and Zn.

الصفات المعدنية والجيوكيميائية للصخور الحديدية في منطقة بنافي شمال العراق

علي طه ياسين و مظفر محمد محمود

المستخلص

تتكون صخور الحديد الرسوبية في منطقة بنافي من أكاسيد وهيدروكسيدات الحديد (هيمتايت، كوثايت، لايمونايت ومكنتايت) وكبريتيدات الحديد (البايرايت والارسينوبايرايت) والمعادن الكاربوناتية (كالسايت، سدرايت وانكرايت) ومن المعادن السليكاتية (كاؤولينايت، جاموسايت، كلوغونايت) فضلا عن الكوارتز والأبتايت. ان معادن الحديد الرئيسة هما الهيمتايت والغوثايت اللذان يتواجدان بنسب عالية نسبيا بالمقارنة مع المعادن الحديدية الاخرى الموجودة في هذا الترسب وان الغوثايت عادة ما يكون ناتج من اكسدة البايرايت والسدرايت والجاموسايت التي حصلت تحت ضروف التجوية بعد بروز هذا الترسب وانكشافه. ان الكالسايت هو المعدن السائد في هذه الصخور وعادة ما يكون غير نقي ويحتوي على الحديد والمغنيسيوم في بنيته البلورية. الكاؤولينايت والجاموسابت هي المعادن الطينية الرئيسية المنتشرة في هذا الترسب اما الغلوكونايت فتواجده نزير جدا. يوجد معدن الارسينوبايرات في النطاق السفلي لهذه الترسبات ذو اللون الرصاصي الغامق حقليا ومرتبطا مع معادن الاباتايت والبايرايت والجاموسايت والغلوكونايت. بناءا على المواصفات الجيوكيميائية للصخور الغنية بالحديد في منطقة بنافي فان نسب تركيز الحديد تتراوح ما بين 3.28 – 33.9 % وبمعدل 20.44% لذا فأنها تعتبر صخور حديدية واطئة المحتوى. ان العلاقة السالبة القوية مابين أوكسيدي الكالسيوم والحديد تعزى الى إحلال المعادن

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الحديدية محل المكونات الكلسية لذا فإنه يمكن ان تصنف هذه الصخور كخامات متكونة بعد الترسب حيث تكونت بسبب عمليات الاحلال التحويرية للصخور الكاربوناتية وهذا ما تؤيده العلاقات السالبة لاوكسيد الكالسيوم مع اكاسيد السليكا والالومينا والفوسفيت وعناصر الكوبلت والنيكل والخارصين والتي تعكس شدة التاثيرات التحويرية في هذه الصخور.

INTRODUCTION

The Benavi ironstone deposit is located about (20) Km (N – NW) of Amadia town in the Duhok Governorate – Northern Iraq (Fig.1). It occurs as an elongated E – W body within Jurassic – Cretaceous sequences and extends for about (2) Km. The exposed thickness of the Benavi ironstone deposit ranges (2.5 – 12.8 m), enclosed within highly fractured carbonate bed. The ironstone is composed of oval to elliptical greenish – yellow oolites of iron minerals (limonite, goethite and hematite) associated with limestone breccia.

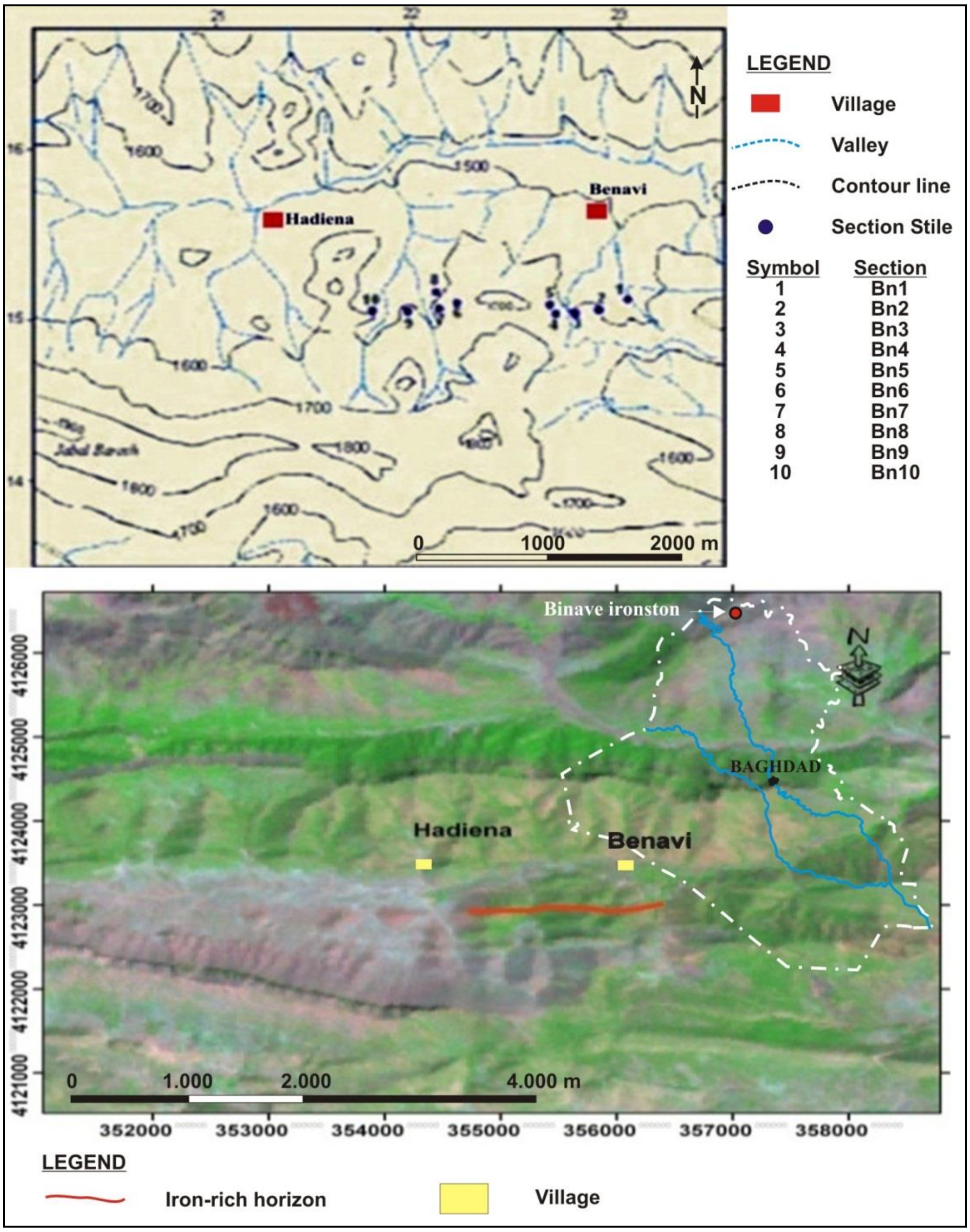

Fig.1: Location of the Benavi ironstone deposit, topographic map of the studied sections and the satellite image of the area showing the continuity of the mineralization

Very little work has been done in this area; no boreholes were drilled to investigate the subsurface extensions of the ironstone mineralization and there is lack of academic research, especially those regarding mineralization. However, occurrences of sedimentary iron ores near Benavi and Hadiena villages are reported by several pioneer geologists. Wetzel (1950) showed that the Hadiena Formation consists of angular fragments of hematite in a matrix of ferruginous limestone in the type locality south of Hadiena village in Amadia district, northern Iraq. McCarthy (1955) described this deposit as a ferruginous grit horizon, (5 – 6 m thick) extending for more than (1 Km) and occurs in the Chia Gara Formation in the area between Hadiena and Benavi villages. Boukhtoyarov and Yevlentyev (1962) described the horizon as hematitic sandstones (6 m) in thickness. Chaikin (1970) showed that the ore-bearing horizons are broken by sublongtitudinal fractures. He proved that the ore deposit is a basal horizon for the Cretaceous sediments, and it is related to the Neocomian transgression. Vanecek (1970) showed that the Benavi ironstone is a bed of fine grained limestone with hematite, the iron content is not very high, but should be satisfactory for industrial use due to the carbonate character of the ore and iron content (about 25 – 30 wt.%). He mentioned that this ore body is the biggest of its type in northern Iraq and recommended to dig trenches at distances of (500 m) apart. Geozavod (1981) carried out reconnaissance exploration work in the Benavi deposit which included chemical analysis of the ore and preliminary reserve estimation. Yassin (2009) classified this deposit as a low-grade Phanerozoic ironstone deposit depending upon geochemical and mineralogical criteria. This review paper is based mainly on results reported by Yassin (2009) and Yassin and Mahmoud (2012).

The results presented in this review paper are based on 48 samples collected from ten sections representing the exposed part of the Benavi ironstone deposit (Yassin, 2009). The sampling is carried out according to variations in color, hardness, texture and iron content. The samples were investigated using ore microscopy, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectrometry (EDS), Thermal Gravimetric Analyses (TGA) and Fourier Transform Infrared Spectrometry (FTIR), (Yassin and Mahmoud 2012). Fifteen Samples have been appropriately selected for SEM observations and EDS analyses. The geochemical characteristic of the Benavi ironstone is investigated through the analyses of (28) samples comprising the whole iron body. The analysis was carried out at Iraq Geological Survey (GEOSURV) using standard work procedures of the survey.

GEOLOGICAL SETTING

Morphologically, the Benavi area is one of three major mountain ranges in Amadia district and runs along the Turkish border in sublongtitudinal direction. The mountain range is separated by broad valleys which are with hilly ground dissected by numerous rivulets and streams. The Benavi ironstone is located in the eastern district of Northern Ora Thrust Zone (Jassim and Goff, 2006). The structural pattern in this zone is characterized by a relatively long, east-west trending anticlinorium with three dome shaped structures, where the oldest Paleozoic rocks are cropping out. The southern limbs of the anticlinorium are the steeper ones. The northern limbs are less disrupted by faults than the southern steeper limbs where the Jurassic – Cretaceous beds are exposed and accompanied by conspicuous thrust fault (Buday and Jassim, 1987). The Benavi ironstone deposit is situated within the Mesozoic formations. According to Hamza and Isaac (1971; in Jassim and Goff, 2006), the outcrop of Benavi ironstone extends over carbonate beds of Chia Gara or Barsarin formations in the Hadiena area, whereas Wetzel (1950) and Geozavod (1981) mentioned that this outcrop is within the Hadiena Formation which is composed of three divisions. The lower division consists of dolomitized limestone with vestiges of conglomeratic and fragmental elements.

The middle division is composed of silty detrital calcareous marls and marly sandy limestone containing detrital hematitic, phosphatic and chert grains. The upper division is composed of conglomeratic and fragmental limestone consisting of angular fragments of hematite in matrix of ferruginous limestone (Buday, 1980). The lower contact of Hadiena Formation is unconformable. The formation overlies mostly the Chia Gara Formation and sometimes the Barsarin Formation. The upper contact of the formation is conformable and gradational; the overlying formation is a dolomitic limestone, considered to be the equivalent of the Aqra Formation (Bellen *et al*., 1959).

MINERALOGY

The Mineralogical investigation of the Benavi ironstones showed that the ore body is composed of several mineral assemblages including iron oxides/hydroxides minerals (hematite, goethite, limonite and magnetite), iron sulfide minerals (pyrite and arsenopyrite), carbonate minerals (calcite, siderite, ankerite), silicate minerals (kaolinite, chamosite and glauconite) in addition to quartz and apatite.

- **Iron oxides/ hydroxides minerals**

– **Hematite:** In the studied samples, hematite is recognized by the X-ray diffraction (XRD) peaks of the reflections: (104): d = 2.69Å and (110): d = 2.51 Å (Fig.2). In the XRD diffractograms the full width on half the maximum (FWHM) are measured. Measurements showed that (FWHM) for the reflection (104) is not doubled (not broader) compared to the reflection plane (110), this indicates that there is no AL^{3+} substitution for Fe^{3+} in the hematite lattice (Al-Youzbaky, 1989), as shown in (Fig.2). The XRD results also show that the hematite content increases upward in the studied sections confirming field observations.

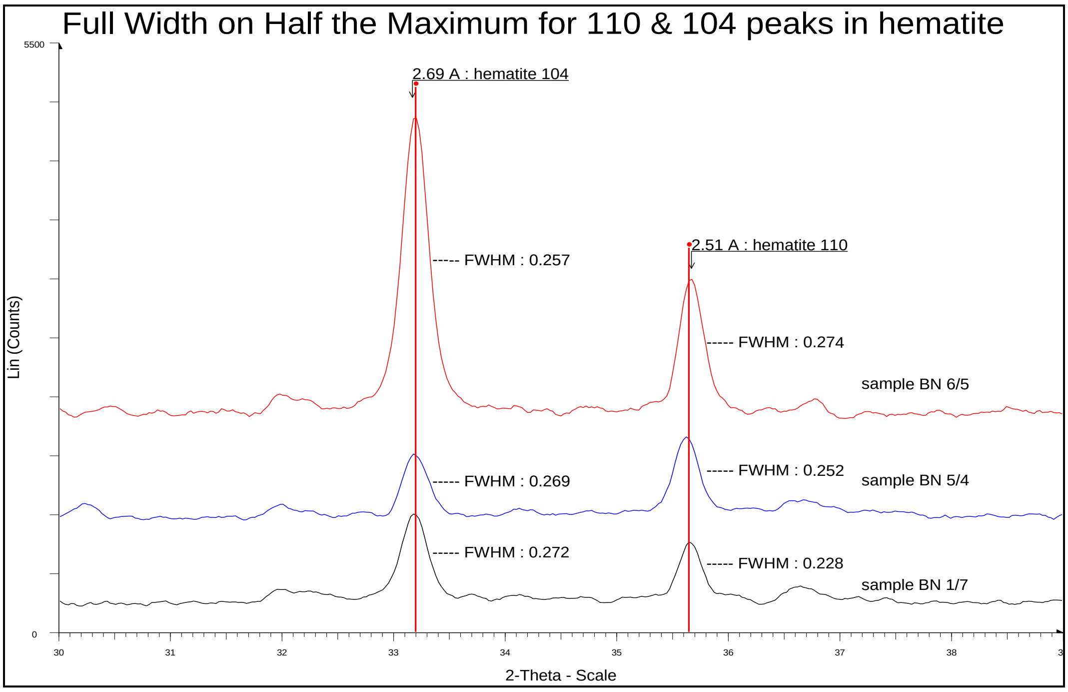

Fig.2: Showing (FWHM) of (110) and (104) peaks in the hematite of some samples (Yassin and Mahmoud, 2012)

– **Goethite:** Goethite is identified by the reflection (110): d = 4.18 Å which is close to the standard value (Fig.3), but the d-space values of reflection (111) are lower than the standard value of (2.448 Å) in most of the ironstone samples. This deviation suggests Al^{3+} substitution for Fe^{+3} in the goethite lattice bringing about shrinkage in the unit cell because Al^{3+} is smaller than Fe^{3+}. Consequently, the XRD peak is shifted to a higher 2θ angles (Al-Youzbaky, 1989) (Fig.3). Goethite is transformed to hematite after heating the samples to (550 °C) due to the dehydration or dehydroxylation of the goethite (Brindely and Brown, 1980).

– **Magnetite:** Magnetite is identified in some of the investigated samples by the reflections: (200): d = 2.96 Å, (400): d = 2.09 Å and (511): d = 1.61 Å. The XRD results verified the ore microscopy study of these samples. Other samples probably contain magnetite but in such limited amounts to be detected by the XRD technique.

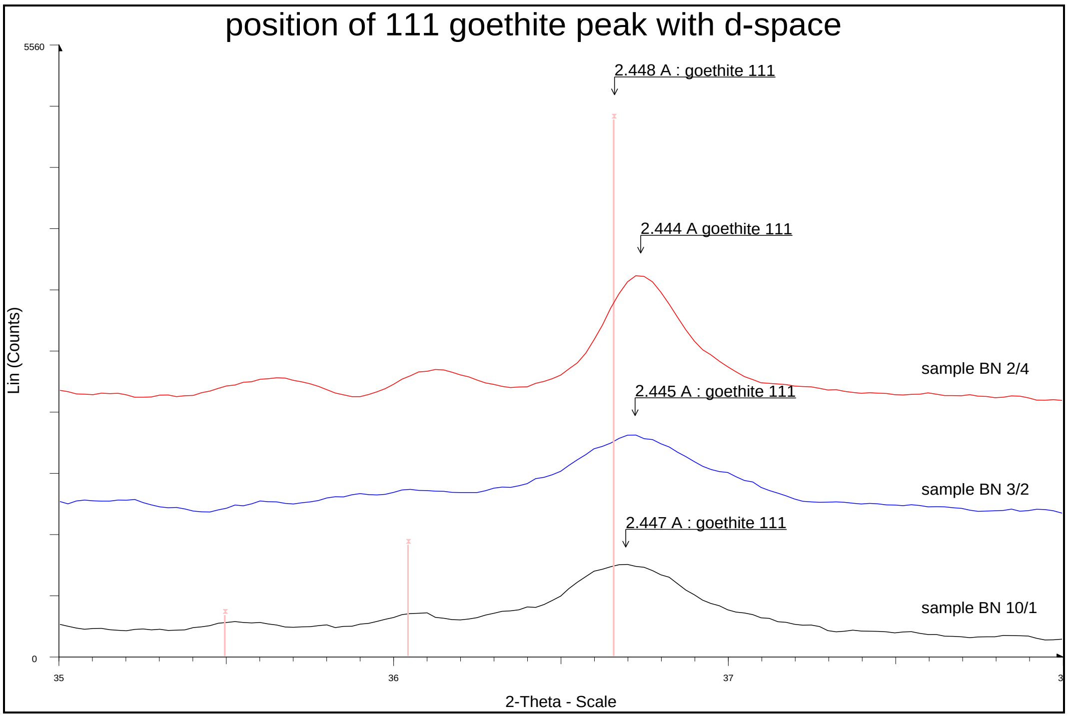

Fig.3: d-space (theoretical and observed) of the plane (111) for goethite (Yassin and Mahmoud, 2012)

- **Sulfide minerals**

– **Pyrite and arsenopyrite:** They are the most important sulfide minerals in the Benavi ironstone (Figs.4 and 5). The only place where arsenopyrite has been reported in Iraq is Marabasta Pb-Zn deposit in the Shalair Terrain of the Zagros Suture Zone (Al-Bassam, 1972). The Marabasta deposit is of Late Triassic – Early Jurassic age (isotope dating), composed of galena, sphalerite, pyrite, arsenopyrite, smithsonite and marcasite. It was later regionally metamorphosed (green schist facies) and some skarn minerals were developed such as magnetite, gahnite and willemite. The Marabasta deposit is hydrothermal in origin, strata-bound and hosted in carbonate rocks (Hak *et al.*, 1983). Arsenopyrite (FeAsS) is identified in the Benavi iron ores by ore microscopic study and confirmed by EDS analyses (Yassin, 2009). Finding arsenopyrite at the base of the Benavi sedimentary ironstone deposit is very interesting, being a mineral usually found in high-temperature hydrothermal sulfide deposits.

- **Carbonate minerals**

– **Calcite, siderite, ankerite and dolomite:** Calcite is predominating whereas siderite and ankerite are minor, and dolomite is trace. Calcite is the main mineral in all samples, identified by the (104) reflection: d = 3.03 Å as well as other less intense reflections. Shifts of the main XRD (104) reflection of calcite compared to the standard value indicate that there is no pure calcite in most of these samples (Figs.5 and 6). The presence of impure calcite is most likely due to Mg^{2+} and Fe^{2+} substitutions in the space lattice of the calcite crystals. This suggestion is supported by the EDS analysis, which shows the presence of Mg and Fe in the calcite spectra. The EDS also showed the presence of ferron-calcite. Siderite ($FeCO_3$) is identified by the (104) reflection: d = 2.79 Å. It is clear there is extremely little shift between the standard main peak value of siderite (104: d = 2.789 Å) and the peak value observed (d = 2.79 Å). Ankerite [$CaMg_{0.27}Fe_{0.73}(CO_3)_2$] is also identified by the (104) reflection: d = 2.90 Å. The standard and observed peak reflections of ankerite are superimposed in the XRD diffractograms of the ironstone samples.

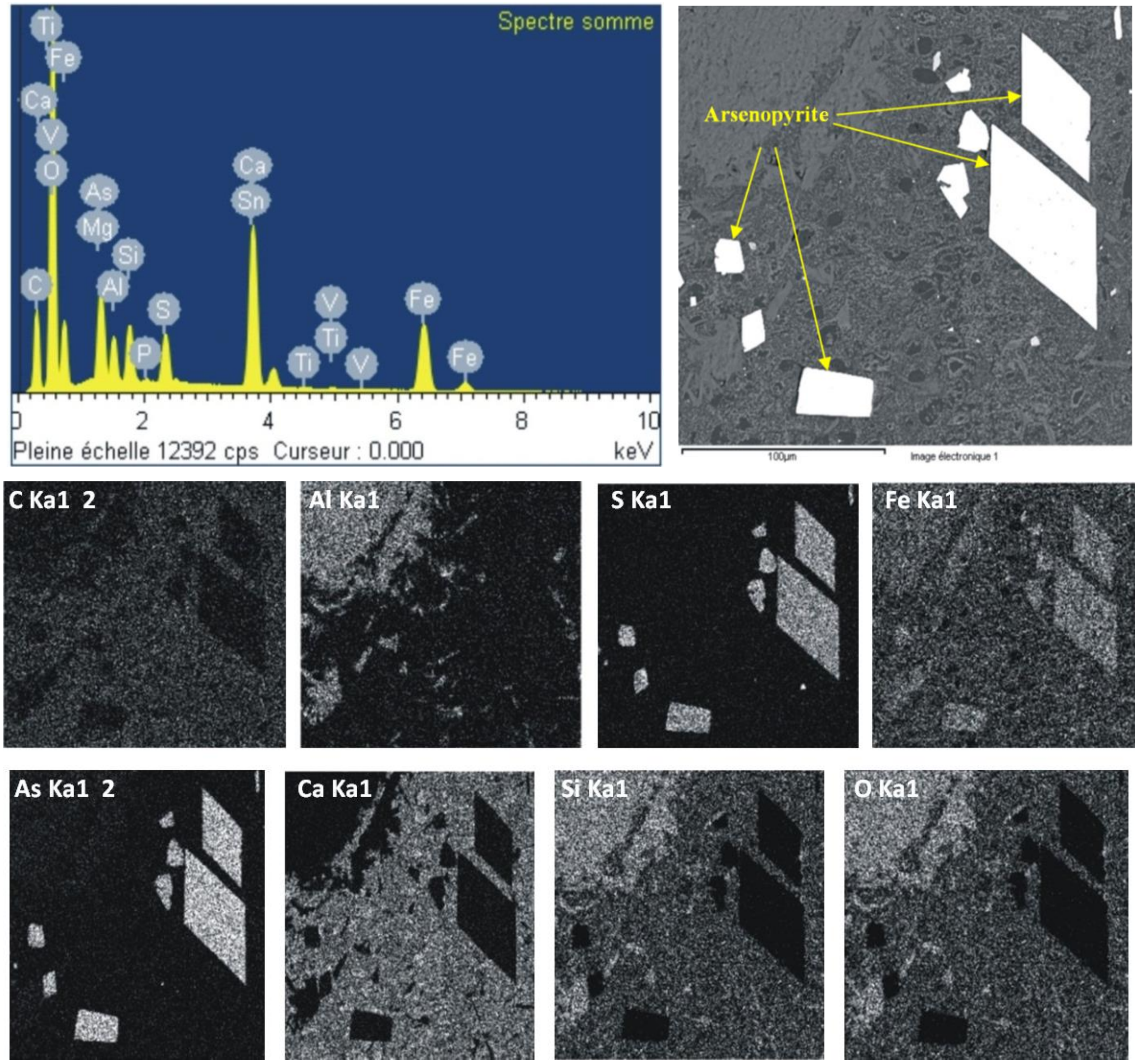

Fig.4: Spectrochemical elements map, BSE image and EDS analysis of arsenopyrite (after Yassin, 2009 and Yassin and Mahmoud, 2012)

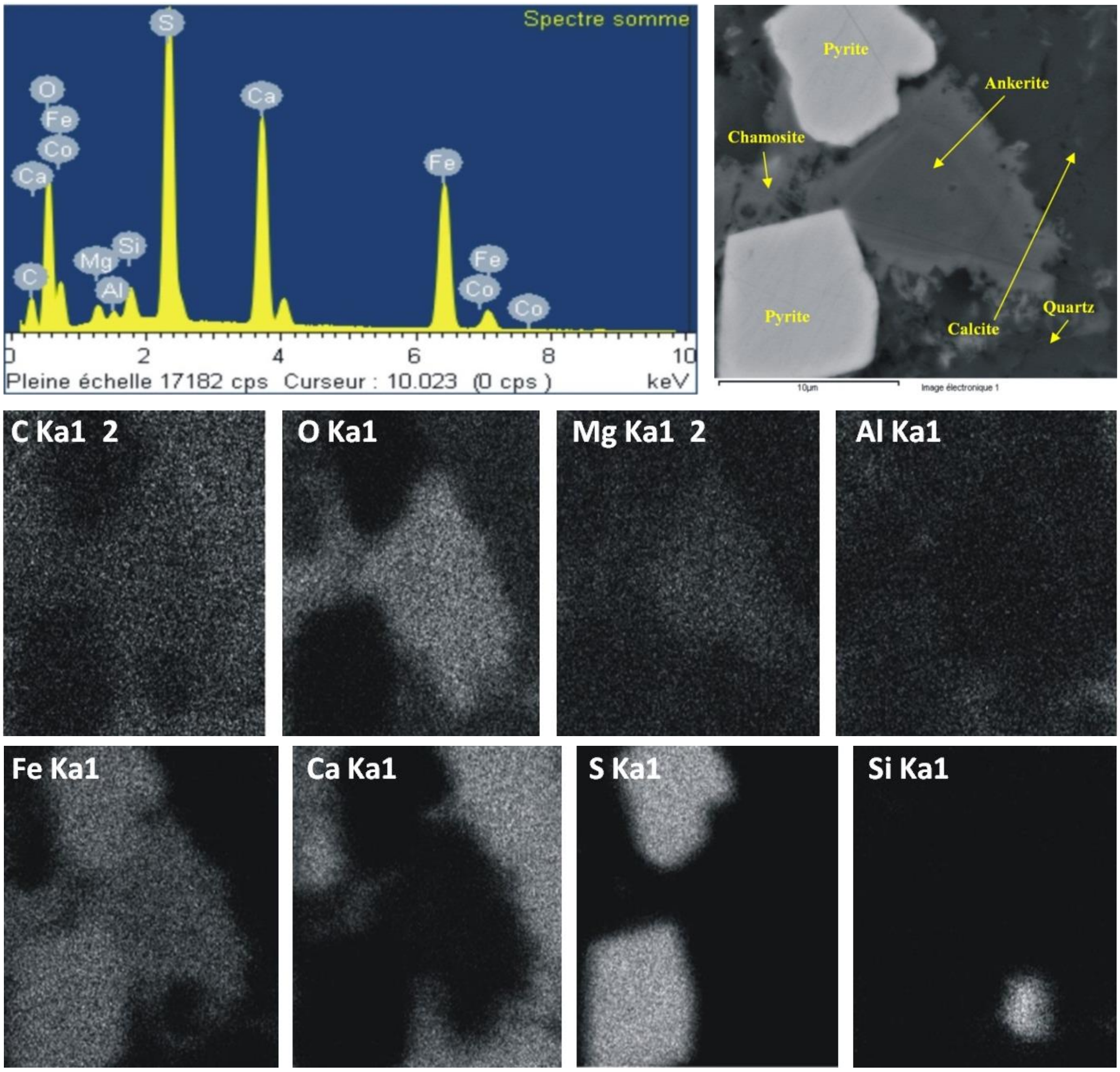

Fig.5: Spectrochemical elements map, BSE image and EDS analysis of ankerite, pyrite, chamosite, calcite and quartz (after Yassin and Mahmoud, 2012)

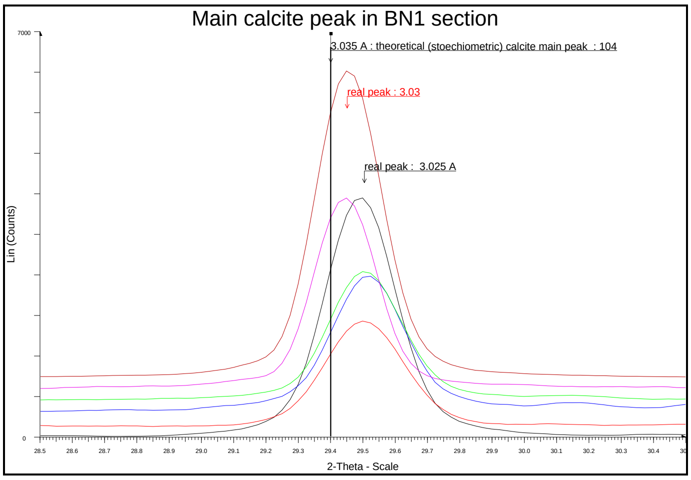

Fig.6: Shows the shift between the observed and theoretical calcite peak of the (104) reflection (Yassin and Mahmoud, 2012)

- **Silicate and phosphate minerals**

Chlorite (chamosite), and kaolinite are the most common silicate minerals identified in many of the ironstone samples (Figs.7 and 8) and Apatite (francolite) is the only phosphate mineral identified in the Benavi ironstone deposit (Fig.9). Free silica (quartz) is a common accessory mineral in these ironstones.

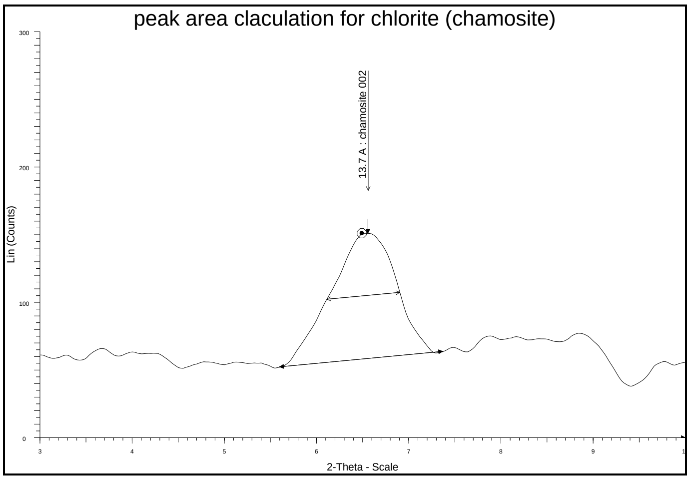

Fig.7: XRD diffractogram of chamosite
(Yassin and Mahmoud, 2012)

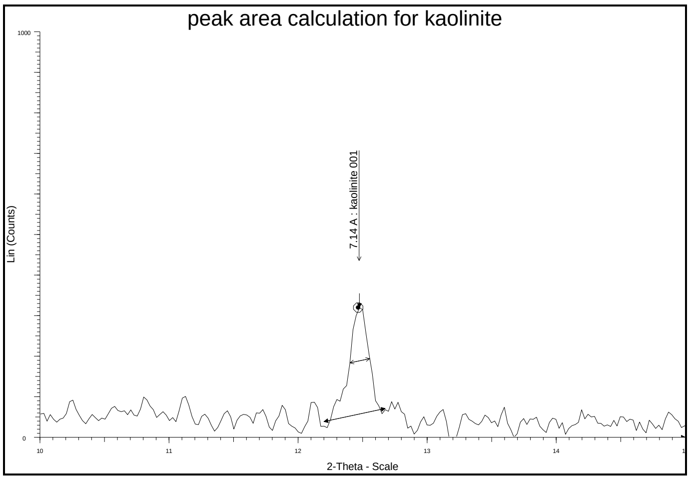

Fig.8: XRD diffractogram of kaolinite
(Yassin and Mahmoud, 2012)

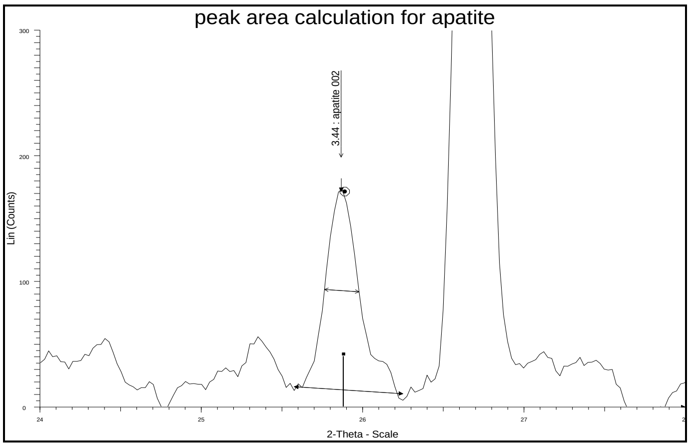

Fig.9: XRD diffractogram of apatite (francolite)
(Yassin and Mahmoud, 2012)

GEOCHEMISTRY

The results of the geochemical analyses for the major oxides in (wt.%) and the trace elements in (ppm) are given in Tables 1 and 2, respectively. The chemical analyses show that Fe_2O_3 ranges (3.28 – 33.9 wt.%) with an average of (20.44 wt.%), which is considered as low-grade ironstones. The correlation coefficients of major and trace elements of Benavi ironstone (Table 3) clearly show the negative relations between the iron oxides with many other oxides (e.g., CaO, SiO_2, Al_2O_3, P_2O_5) and elements (e.g., Co, Ni, and Zn) suggesting Fe-replacement process. The geochemical results are in agreement with the mineralogy of the samples and explain the various diagenetic processes that have influenced this ironstone deposit.

Table 1: Bulk chemical analyses of Benavi ironstone for major oxides (wt.%) with minimum (Min), maximum (Max) and average (Av) values (Yassin, 2009)

	Sample	**SiO_2**	**Fe**	**Fe_2O_3**	**FeO**	**Al_2O_3**	**TiO_2**	**CaO**	**MgO**	**L.O.I.**	**Na_2O**	**K_2O**	**P_2O_5**
		%											
1	BN1/1	1.05	2.20	3.28	2.01	0.53	0.18	51.83	0.98	41.76	0.10	0.01	0.21
2	BN1/4	4.02	10.30	14.56	10.57	1.94	0.19	42.33	2.30	33.30	0.14	0.02	0.99
3	BN1/5	3.30	17.43	24.90	16.65	1.56	0.15	35.92	2.35	29.12	0.12	0.01	0.88
4	BN1/6	2.84	17.00	23.90	5.38	1.60	0.15	37.51	1.10	30.14	0.16	0.03	1.13
5	BN1/7	4.24	17.00	24.00	1.00	1.53	0.13	36.96	0.67	29.11	0.12	0.02	1.37
6	BN2/4	2.76	10.00	14.00	1.43	1.29	0.10	43.68	0.72	35.48	0.11	0.03	1.01
7	BN2/5	7.40	16.00	22.80	2.36	3.78	0.28	33.60	1.20	28.45	0.13	0.06	1.16
8	BN2/6	3.48	13.00	17.90	1.00	0.99	0.15	41.21	0.64	33.70	0.12	0.11	1.23
9	BN2/7	3.82	18.06	25.80	4.16	1.63	0.15	36.14	0.83	28.73	0.12	0.07	1.15
10	BN2/8	3.60	15.20	21.70	0.93	1.16	0.11	39.54	0.71	31.18	0.12	0.10	1.33
11	BN3/2	4.50	9.00	12.25	1.93	2.03	0.19	42.00	2.20	35.40	0.22	0.17	0.40
12	BN3/4	4.08	20.10	28.70	1.65	1.60	0.14	34.92	0.50	26.16	0.26	0.07	1.60
13	BN4/1	3.98	18.13	25.90	1.07	1.56	0.13	36.68	0.48	28.55	0.12	0.07	1.31
14	BN5/1	2.27	3.00	4.06	2.36	0.83	0.06	50.38	0.92	40.16	0.10	0.04	0.50
15	BN5/2	5.02	10.00	13.60	1.93	1.82	0.16	40.93	2.45	35.00	0.21	0.17	0.64
16	BN5/3	3.74	15.30	21.80	3.01	1.44	0.18	37.52	1.34	30.72	0.11	0.03	1.61
17	BN5/4	2.68	17.10	24.40	5.52	1.35	0.13	37.87	0.98	29.83	0.11	0.02	1.07
18	BN6/3	6.02	20.00	27.80	1.43	2.93	0.23	32.48	0.66	28.26	0.15	0.21	0.96
19	BN6/4	2.00	12.11	18.20	0.93	0.94	0.06	42.56	0.44	34.01	0.11	0.03	0.53
20	BN6/5	3.48	23.40	33.90	1.20	1.75	0.13	33.40	0.36	26.02	0.14	0.08	0.93
21	BN7	2.32	14.00	19.60	1.34	1.13	0.09	42.00	0.59	32.08	0.13	0.06	1.23
22	BN8/2	2.80	4.40	6.22	4.33	1.04	0.06	48.05	1.50	39.22	0.12	0.02	0.57
23	BN8/4	5.92	14.10	20.10	0.92	1.89	0.19	37.52	0.65	29.64	0.12	0.04	2.08
24	BN8/5	3.38	22.00	31.20	1.13	1.69	0.13	34.16	0.52	26.96	0.20	0.08	1.63
25	BN9/1	3.90	10.00	13.85	11.00	1.46	0.13	40.66	2.35	36.69	0.10	0.02	0.47
26	BN9/3	2.92	21.00	29.80	1.91	1.65	0.11	35.00	0.55	26.62	0.12	0.03	1.25
27	BN10/1	7.36	14.10	20.10	2.84	4.13	0.30	34.26	1.06	29.81	0.19	0.09	0.84
28	BN10/3	2.96	20.00	28.00	0.71	1.60	0.11	37.52	0.47	27.86	0.11	0.05	0.97
	Min.	1.05	2.20	3.28	0.71	0.53	0.06	32.48	0.36	26.02	0.10	0.01	0.21
	Max.	7.40	23.40	33.90	16.65	4.13	0.30	51.83	2.45	41.76	0.26	0.21	2.08
	Av.	3.78	14.43	20.44	3.24	1.67	0.15	39.15	1.05	31.57	0.14	0.06	1.04

Table 2: Bulk chemical analyses of trace elements in (ppm) and Mn/Fe ratios, of Benavi ironstone with Minimum (Min), Maximum (Max) and Average (Av.) values (Yassin, 2009)

	Sample	**S**	**Mn**	**Zn**	**Co**	**Ni**	**Cr**	**Mn/Fe**
		ppm						
1	BN1/1	47.50	73.00	23.00	18.00	18.00	305.00	0.0032
2	BN1/4	1700.00	134.00	54.00	24.00	30.00	729.00	0.0013
3	BN1/5	107.60	131.00	46.00	26.00	30.00	1044.00	0.0008
4	BN1/6	44.30	145.00	41.00	24.00	28.00	1445.00	0.0009
5	BN1/7	20.60	135.00	31.00	22.00	21.00	570.00	0.0008
6	BN2/4	33.50	141.00	62.00	23.00	27.00	771.00	0.0014
7	BN2/5	131.80	184.00	75.00	24.00	33.00	1145.00	0.0012
8	BN2/6	79.00	154.00	44.00	24.00	25.00	455.00	0.0012
9	BN2/7	0.00	144.00	36.00	28.00	31.00	668.00	0.0008
10	BN2/8	0.00	152.00	34.00	24.00	27.00	577.00	0.0010
11	BN3/2	0.00	133.00	28.00	22.00	27.00	75.00	0.0016
12	BN3/4	0.00	154.00	37.00	24.00	25.00	627.00	0.0008
13	BN4/1	53.40	148.00	41.00	22.00	25.00	714.00	0.0008
14	BN5/1	95.90	100.00	17.00	21.00	24.00	99.00	0.0035
15	BN5/2	37.60	131.00	21.00	23.00	28.00	280.00	0.0014
16	BN5/3	23.30	215.00	41.00	28.00	33.00	578.00	0.0014
17	BN5/4	108.40	146.00	29.00	26.00	29.00	683.00	0.0009
18	BN6/3	57.10	194.00	56.00	37.00	34.00	775.00	0.0010
19	BN6/4	57.00	141.00	21.00	22.00	25.00	558.00	0.0011
20	BN6/5	160.20	180.00	28.00	25.00	25.00	1246.00	0.0008
21	BN7	103.70	118.00	25.00	22.00	23.00	599.00	0.0009
22	BN8/2	1200.00	38.00	36.00	22.00	22.00	92.00	0.0009
23	BN8/4	77.60	54.00	52.00	29.00	53.00	573.00	0.0004
24	BN8/5	22.40	43.00	40.00	25.00	30.00	809.00	0.0002
25	BN9/1	1500.00	65.00	61.00	24.00	25.00	3305.00	0.0007
26	BN9/3	67.00	36.00	32.00	27.00	27.00	799.00	0.0002
27	BN10/1	59.20	22.00	20.00	26.00	31.00	709.00	0.0002
28	BN10/3	208.30	159.00	41.00	28.00	28.00	755.00	0.0008
	Min.	0.00	22.00	17.00	18.00	18.00	75.00	0.0002
	Max.	1700.00	215.00	75.00	37.00	53.00	3305.00	0.0035
	Av.	214.12	123.93	38.29	24.64	28.00	749.46	0.0011

Table 3: Correlation coefficients of major and trace elements of Benavi ironstone (Yassin, 2009)

	SiO_2	**Fe**	Fe_2O_3	**FeO**	Al_2O_3	TiO_2	**CaO**	**MgO**	**L.O.I.**	Na_2O	K_2O	P_2O_5	**S**	**Mn**	**Zn**	**Co**	**Ni**	**Cr**
SiO_2	1.00																	
Fe	0.25	1.00																
Fe_2O_3	0.24	1.00	1.00															
FeO	-0.06	-0.10	-0.10	1.00														
Al_2O_3	0.90	0.32	0.32	0.00	1.00													
TiO_2	0.80	0.14	0.13	0.07	0.84	1.00												
CaO	-0.58	-0.92	-0.92	0.01	-0.62	-0.44	1.00											
MgO	0.16	-0.44	-0.45	0.71	0.11	0.23	0.23	1.00										
L.O.I.	-0.39	-0.97	-0.97	0.10	-0.44	-0.26	0.95	0.40	1.00									
Na_2O	0.38	0.22	0.21	-0.15	0.38	0.32	-0.32	0.15	-0.27	1.00								
K_2O	0.48	0.16	0.14	-0.38	0.39	0.35	-0.28	0.04	-0.14	0.55	1.00							
P_2O_5	0.28	0.62	0.62	-0.24	0.13	0.11	-0.58	-0.45	-0.69	0.11	-0.06	1.00						
S	-0.03	-0.35	-0.35	0.55	-0.05	-0.08	0.28	0.53	0.34	-0.18	-0.13	-0.29	1.00					
Mn	0.05	0.31	0.31	-0.09	0.01	0.08	-0.27	-0.09	-0.28	-0.04	0.26	0.14	-0.26	1.00				
Zn	0.39	0.18	0.17	0.29	0.32	0.33	-0.30	0.15	-0.20	-0.17	-0.07	0.30	0.33	0.24	1.00			
Co	0.46	0.58	0.56	0.03	0.45	0.36	-0.65	-0.14	-0.57	0.03	0.37	0.39	-0.10	0.24	0.37	1.00		
Ni	0.58	0.27	0.27	0.03	0.44	0.45	-0.44	0.01	-0.38	0.05	0.13	0.56	-0.10	-0.01	0.41	0.63	1.00	
Cr	0.11	0.24	0.24	0.47	0.15	0.09	-0.32	0.22	-0.17	-0.17	-0.23	-0.03	0.42	-0.04	0.50	0.15	0.04	1.00

(r = 0.38)

ORIGIN

According to the petrological and geochemical analyses of the studied samples, the sedimentary epigenetic origin of the Benavi ironstone deposit is confirmed. Iron content of the carbonate rocks is commonly increases during diagenesis (Maynard, 1983). The very strong negative relationship between calcium and iron is attributed to the replacement of calcareous constituents by iron minerals during diagenesis (Babalola *et al*., 2003). The origin of the Benavi ironstone deposit can be considered as epigenetic ore formed by the diagenetic replacement of carbonate rocks in the manner described by Selley (2007).

The relationship of the minerals comprising the iron ore body throws some light on the diagenetic history. The XRD results show negative relationship between calcite and iron oxides/ hydroxides in the Benavi ironstone. This is probably due to the loss of carbonate which took place during the oxidation of ferrous iron to ferric iron and release of H^{1+}, where the initial calcite was dissolved and replacement of iron oxides/ hydroxides occurred. The later minerals have probably undergone structural transformation when entering an anoxic environment. These diagenetic transformations are investigated by many researchers where high specific surface area of iron oxides/ hydroxides act as important sorbents to dissolve mineral species, particularly heavy metals, phosphates and arsenate. Then, under reducing conditions, most of the adsorbed species is released from iron oxides/ hydroxides surfaces (Pedersen, 2006). This may give a clue about the presence of phosphate minerals in the studied samples, as well as the presence of arsenopyrite in the lower part of the iron body in the Benavi deposit.

The negative relationship observed between chamosite on one hand and kaolinite and iron oxides/ hydroxides on the other hand, may provide some indication on the formation of chamosite from kaolinite and iron oxides/ hydroxides under reducing conditions (Gartner and Schellmann, 1965). Kaolinite may be recrystallized or transformed to chamosite under reducing conditions in the availability of Mg^{+2} and iron oxides (Mucke and Farshad, 2005). On the other hand, the negative relationship observed between chamosite and iron oxides/ hydroxides is good evidence supporting oxidized chamosite to form goethite under weathering circumstances beyond exposure of ironstone (Taylor, 1949).

The XRD analysis shows the presence of Al-poor hematite and Al-rich goethite, whereas TGA proved the presence of two types of goethite with different Al contents (Al-rich and Al-poor goethite). The Al-poor hematite was most probably originated by dehydration of primary Al-poor goethite in the absence of water or elevated temperatures. On the other hand, Al-rich goethite (secondary goethite) was probably produced by the weathering processes which caused oxidation of chamosite and pyrite as well as probably siderite. The goethitization process may have occurred after exposure of the Benavi ironstone; Kampf and Schwertmann (1983) reported that Al-substitution in goethite relates positively with surface weathering circumstances. The SEM and EDS analyses clearly show the oxidation of pyrite and chamosite. This yield clues to the source of goethite in the studied ironstone and explains the yellow and yellowish brown color of the ironstone deposit at its middle part.

The relatively high concentrations of Ti, Cr, P and Al support the sedimentary origin of the deposit since hydrothermal solutions originating from volcanic activities are poor in these elements (Tobia, 1983). Furthermore, there are no evidences for volcanic activities in Benavi deposit and the adjacent areas. The modicums of Pb, Zn and Cu also indicate the sedimentary origin (James, 1966 and Harder, 1978). High As in the pyrite of Benavi ironstone may be considered supporting evidence of the sedimentary origin (Khaldoun Al-Bassam, personal communications).

The origin of arsenopyrite in the Benavi ironstone is debatable, as there are many possibilities for the formation of this mineral in this deposit. The large and well-formed crystals of arsenopyrite seem typical of hydrothermal origin and suggest some hot fluids that were probably involved (David Alderton, personal communication). But this suggestion may not be appropriate in the case of the Benavi deposit. There are other possibilities which are probably more satisfactory. In acidic environments, the oxides surfaces are positively charged causing adsorption of anions (Cornell and Schwertman, 2003) where the adsorbed arsenic may be mobilized with phosphate. These adsorbed anions may also be released upon reduction of iron oxides because the available surface area decreases, thus, reduction of iron oxides has been also suggested as a mechanism for arsenic oxyanions $(AsO_4)^{3-}$ and phosphates release (Pedersen, 2006). This is probably the case occurred in the Benavi ironstone deposit and explains the occurrence of phosphates in the ore deposit in association with pyrite and arsenopyrite. Arsenic concentrations were probably more than enough to form As-rich pyrite and the access As may have formed arsenopyrite during the reduction stage, and/ or the arsenic might have been derived from the As-rich pyrite which has undergone oxidation and combined with the sulfur released from altered pyrite to form authigenic arsenopyrite crystals (Yawooz Kettanah, personal communication).

Most of the primary sulfide ores (pyrite) were altered to secondary ores (goethite) by influence of supergene solutions (Awadh *et al*., 2008). This suggestion is supported by ore microscopy study and SEM analyses which showed the presence of arsenopyrite restricted chemically to the richest samples in S and FeO, and mineralogically to the richest samples in pyrite. The ferruginization process probably occurred by descending solutions that caused dissolution, migration and precipitation of various elements depending on prevailing Eh/pH conditions. The ferruginization appears to be an important phenomenon in the Cretaceous times, when the Benavi ironstone deposit was developed (Mucke and Farshad, 2005).

ECONOMIC POTENTIAL

There is little information to assess the real potential of the Benavi ironstone deposit as economic source material for iron. The only work in this respect is that of Geozavod (1981) who carried out reconnaissance exploration in the Benavi area as they were mapping and investigating the Duri Serguza Zn-Pb-pyrite deposit in the nearby vicinity. They have examined the surface exposure of the iron ore deposit occurring as an elongated E – W body 2.2 Km long and (15 – 30) m thick within Jurassic – Cretaceous sequence. The ironstone is composed of oval to elliptical greenish – yellow oolites of iron minerals (limonite, goethite and hematite) associated with limestone breccia. The chemical analysis shows (in wt.%): Fe_2O_3 (17.8 – 26.2), CaO (27.4 – 32.7), SiO_2 (4.4 – 4.94), Al_2O_3 (2.05 – 2.49), P (0.21 – 0.43) and S (0.12 – 0.21). The geological reserve was estimated by (15 – 20) m.t. (Geozavod, 1981). However, the extension of the deposit in subsurface was never investigated. The importance of the Benavi ironstone deposit lies in the carbonate gangue minerals making the main impurity of the ore. Carbonates can be easily removed by simple ore dressing techniques, which can render a high-grade iron ore concentrate. At the present time, the deposit can serve as a raw material for cement industry.

CONCLUSIONS

The Benavi ironstone deposit can be considered as a low-grade ironstone deposit with Fe_2O_3 content ranges between (3.28 – 33.90 %) with the average of (20.44%). The ironstone is mainly composed of hematite, goethite with minor limonite and magnetite. The sulphides are not common and present as pyrite and arsenopyrite. Calcite is the major component of the carbonate minerals with minor siderite and ankerite. Kaolinite, chamosite and glauconite, in addition to quartz and apatite are minor. Two types of goethite are found which differ in crystallization and Al-content; The Al-rich goethite is a secondary mineral, produced by the oxidation of pyrite, siderite and chamosite under surface weathering. Hematite is mostly an Al-poor type, originated by the dehydration of primary Al-poor goethite. Chamosite is formed from kaolinite under reducing conditions in the availability of Mg^{2+} and presence of iron oxides. The origin of arsenopyrite is controversial, but most probably it was formed later in reducing environment, following the earlier oxidation of pyrite and release of arsenic. Arsenic content is high in pyrite of the Benavi ironstone and goethite produced by the oxidation of pyrite is characterized by unusually high As content. The iron ores at the Benavi deposit were formed by epigenetic replacement of calcareous constituents by iron minerals. The deposit may be useful as a raw material in cement industry and deserves further exploration, especially in subsurface.

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