



Islamic Azad University  
Mashhad Branch

# Paragenesis and geochronological studies of Asnawa Iron Ore by the isotope and mineral chemistry in Penjween Area, Zagros Suture Zone Kurdistan Region, NE Iraq

Kamal H. Karim<sup>\*1</sup>, Nabaz R.H. Aziz<sup>1</sup>, Mayssa A. A.A Al-Bidary<sup>2</sup>

1. Department of Geology, University of Sulaimani, Kurdistan Region, Iraq

2. Department of Geology, University of Baghdad, Iraq

Received 2 October 2014; accepted 27 February 2015

## Abstract

The Asinawa iron ore is located about 3km to the southeast of Penjween town, Sulaimaniya Governorate, Kurdistan Region, Northeastern Iraq near the Iraq-Iran border. The exposed iron ore deposit is about 60 and 400m wide and long respectively. The present study is the re-study of the geology and geochemistry of the Asnawan Iron ore deposit and concluded that the country rocks are consist of hornfels in which the original lamination or banding of the parent rocks (calc-silicate low grade metamorphic rocks) are preserved and inherited from its laminated sedimentary precursors. Moreover, the facies that is associated with host rocks is hornblende-hornfels facies with temperature range of 550-650 °C. This range is confirmed through thermo barometry. There are evidences of localized pyroxene-hornfels and sanidine hornfels facies too. Additionally, the detail of the different stages of the iron ore paragenesis is shown by discussion with the aid of suitable graphical drawing and geochemical variation diagrams. By these methods, the sedimentary stratigraphic unit of the parent rock (protolith) was found for the first time which consists of Qulqula Radiolarian Formation (Kermanshah Radiolarites in Iran). The bedded chert, limestone and calcareous shale is the main lithology of the latter formation and after burial and deformation, it is regionally metamorphosed to banded and lamiated calc-silicate rocks of green facies rocks. At a later stage, these rocks, remetamorphosed (polymetamorphism pattern) again to hornfels with concurrent changing to iron ore by basic iron rich hydrothermal solutions during Eocene (37-40Ma). This age is calculated using  $Ar^{39}/Ar^{40}$  method of dating.

**Keywords:** Asnawa iron ore, Qulqula Radiolarian Formation, hornfels, skarn, Penjween mineralization, paragenesis

## 1. Introduction

The Asnawa iron ore is located near the Iraq-Iran border, about 3 km to the southeast of Penjween Town, which has been identified as an important metallogenic province of the northeastern Iraq (Jassim et al. 1982). The studied area occupies part of the Iraqi Zagros Suture Zone (Fig. 1). The previous ideas about the origin of the iron ore and its country rocks were controversial. One idea suggested metasomatic replacement of calc-silicate schist (as country rocks) by iron ions which are derived from alteration of nearby diorite body. Another one suggested metasomatism replacement of gabbro, as country rock, by hydrothermal iron rich solution. These ideas suggest that the replacement was occurred in relatively low temperature which was in the range of green schist facies (Pshdari 1983; Al-Bidary 2011).

The iron ore occurs as contact skarn ore deposit near the Penjween Town; the largest one is the Asnawa ore deposit which is exposed along four small quarries on a steep, north-east facing slopes of a border mountain

peak known as Asinkolen. The preliminary study of Asnawa iron ore deposit was done by Site Investigation Co. (UK) during the fifties of the last twenty century and then followed later by Iraqi Geological Survey as a comprehensive investigation projects.

McCarthy (1965) investigated Asnawa iron ore which is situated in a complex zone of igneous and metamorphic rocks of uncertain age. Bolton (1958) had indicated that the iron ore was found within metamorphic rocks in the Qandil Series. Teretenko and Teretenko and Khadikov (1961) classified the Asnawa iron mineralization as contact metasomatic and considered that it originated along the contact of diorite intrusion in the carbonates rocks of the Penjween Group while Jassim et al (1982) has consider it as a part of the Penjween Massif. Pashdari (1983) has confirmed occurrence of both exo and endoskarn near the iron ore indicated that the contact rocks (intercalated marble and calc-silicates) around Asnawa are subjected to intense metasomatism. He added that the iron-bearing solutions were generated by alteration of nearby diorite body and the solutions had transformed a silicate exoskarn rocks into limy

\*Corresponding author.

E-mail address (es): [kamal.karim@univsul.edu.iq](mailto:kamal.karim@univsul.edu.iq)

exoskarn and magnetite ore-skarn by main metasomatim. The same idea is confirmed by Aswad and Pshdari (1985) who indicated that the source of iron was mainly came from solutions that are derived from diorite. Al-Bidary (2011) and Yara (2014) have concluded a magmatic origin of the country rock. The reserve of Asnawa iron ore is estimated to be less than 1.5 million tones by McCarthy (1965). Form decays of the last century it is quarried from time to time and few thousand tones are used for improvement of Portland cement. The propose of present study is to achieve genesis and paragenesis of the Asnawa iron ore deposit by the help of mineralogy, geochemistry of the iron ore and the country rocks.

### 1.1. Geology of the studied Area

The study area is consisting of high mountainous terrain of Zagros type which has northwest–southeast trend. Between the mountains, there are low intermountain plains such as Rawgan Plain to the north and northwest of Penjween town. In the area, the highest peak does not exceed 1822 meters while the lowest elevation (such Rawgan plain) is about 400m below this elevation (Teretenko and Khadikov 1961). The iron ore is located at the southeastern end of the Kani Shawqat Mountain which looks over the Penjween town. The peak at this end is called Asin

Kolen Mountain. At this end there is a small v-shaped valley which is called Belkian valley and contains a governmental picnic buildings. The iron ore is located at the head of this valley and exposed on the surface as small bodies along the northeastern side of the latter mountain which is about 1755m high from the mean sea level. The ore body is about 250 m long and 50 m wide and has almost elliptical shape with long direction striking north-south with the base at lower slope (base) of Asin kollen Mountain and its tip nearly coincides with the peak of the mountain (Fig.1 and 2).The ore consists of several north-south trending nearly vertical veins (10cm-2m thick) of different sizes and interlayer with metamorphic rocks. The iron veins are thick or thin and pure near the base of the triangle and have black color with metallic luster. Toward the top, the gangue minerals increase and the iron ore become secondary and dull in lusters which exist as thin discontinuous veins (Fig. 4). The Asnawa mineralized zone is located inside the lower part of Qandil metamorphic group. This group constitutes the main units of the Zagros Suture Zone in the northeastern Iraq. In Penjween area, Penjween Igneous complex (or Penjween Ophiolite Complex) emplace the group and has an outcrop of approximately 35 km<sup>2</sup> within the Iraqi territories. The rest is located within adjacent Iranian territories.

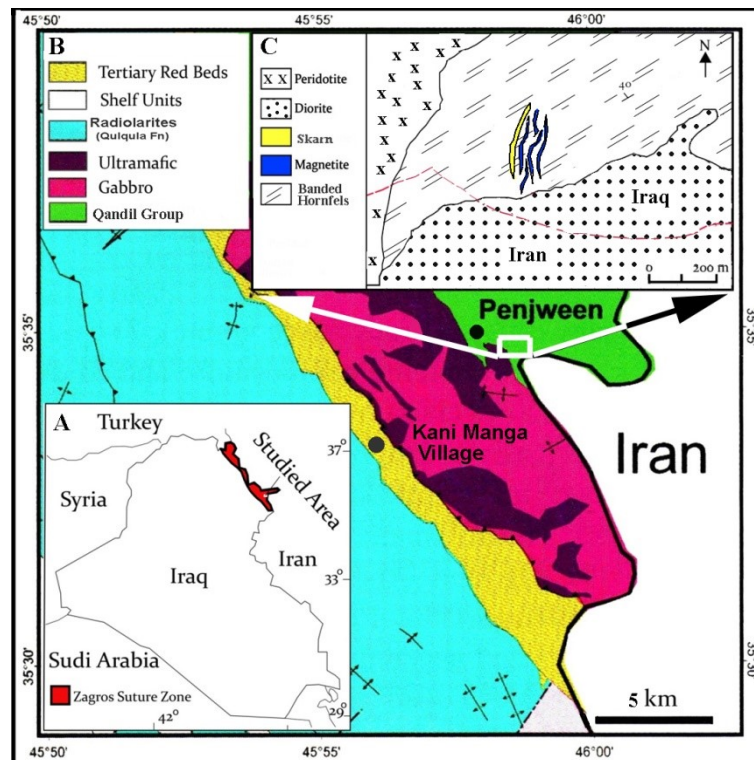


Fig. 1. The figure A shows area under study. Figure B, geological maps of the studied area. Figure C geological map of the Asnawa iron ore in side Qandil Group modified after (McCarthy 1965, Jassim et al. 1982 and Pshdari 1985).

The Asnawa iron ore and the country rocks are intensely shared and located between the diorite body at the east and ophiolite (mainly peridotite and gabbro) at west (Fig. 1). The area around iron mineralization zone is intruded by a large mass of peridotite on the north-west and by a small plug-like body of diorite intrusion on the south and south-east. The siliceous

schist (regionally metamorphosed sedimentary rock of Qandil Unit) is metamorphosed by peridotite and diorite intrusions at the northwest and south respectively (McCarthy 1965). He added that the main mineralized zone lies between the marbles and the calc-silicates and terminated by a north-south trending local faults (Fig. 1).

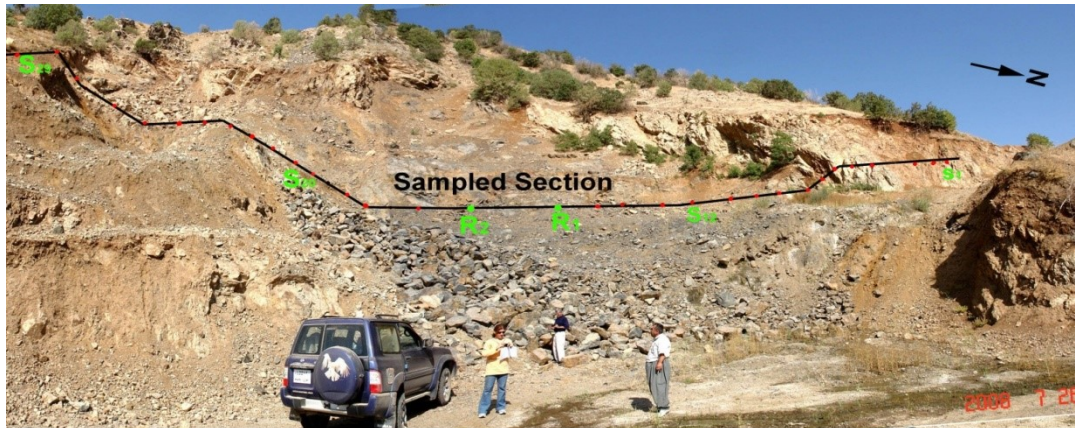


Fig. 2. Lower quarry of the Asnawa iron ore (S1 sampled section) shows location of the samples S1....S29 with two samples of pure iron ore R1 and R2 .

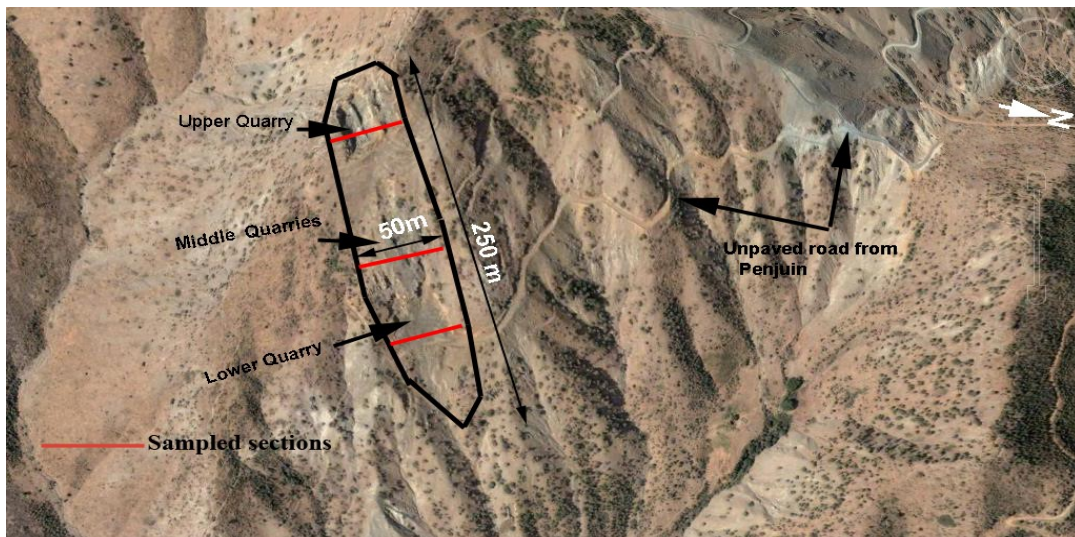


Fig. 3. The three quarries (from Google Earth, 2009) of the Asnawa iron ore and four sampled sections. The Iron exists as veins of 1cm to 4 m thickness



Fig. 4. Upper Quarry of the Asnawa iron ore (S3 samples section) shows partial and veinal replacement of country rocks (banded hornfels) by iron

## 2. Methodology of the and Analytical techniques

The studied of the Asnawa iron ores exposed in four small quarries, a detailed geological study of the whole area is conducted in field for recording relations of all rocks that are related to the iron ore. More than 40 samples are taken from four sections which are representing the whole Asnawa iron ore and its country rocks (Fig. 2, 3 and 4). From these samples thin section are prepared for analyses by various techniques. The geochemical and petrographical analyses of Al-Bidary (2011) are used for this study. Analytical studies of the samples are conducted at the Department of Earth Science, Dalhousie University, Canada. The ICP-MS and INAA techniques are used for the bulk-rock analysis (major, trace and REEs). The mineral chemistry of iron ore and country rocks are determined by an electron microprobe technique using JEOL 8200 microprobe. The operating conditions were 15 kv accelerating potential and 20A probe current.

The age of the country rock and iron ore is determined by Ar-Ar age dating in Dalhousie University/Earth Science department, Canada. In the procedures, the samples are crushed to size of 63 micron. Then wet sieved to remove the clay mineral. The samples are dried in 100 °C oven and Sodium polytungstate heavy liquid diluted to specific gravity 2.89 was used to separate the heavy minerals. Then hornblende is handpicked under microscopy type Olympus SZ61 model SZ2-LGB. Finally a computer controlled VG-3600 high-sensitivity mass spectrometer with Tantalum double vacuum resistance furnace is used for Argon analyses. The samples irradiated for 10 hours at the McMaster nuclear reactor in Canada, and the

system is calibrated using the Fish Canyon tuff sanidine standard with an age of 28.2 Ma. figure 2-16.

## 3. Result

### 3.1. Mineralogy and Mineral chemistry

#### 3.1.1. The iron ore

The iron ore body has spotty and ribbon-like appearance with localized distribution along the area of 50m×250m. It consists of magnetite and other associated minerals and accompanied by gangue minerals which consist mainly of hornblende with minor amounts of clinopyroxene. The magnetite occurs as dense massive or laminated aggregates under the microscope and changes to clear visible banded structure in outcrop. The bands has width of 3mm to 10cm and in rare case exist as large veins, more than 3m thick giving rise to banded structures in the rock (Fig. 4).

The concentrations of Fe<sub>3</sub>O<sub>4</sub> (magnetite) in the iron ore body (samples of pure iron ore R1 and R2 see figure 2) range from 93.98% to 84.74% (see Al-Bidary, 2011, appendix 5, 6 and 7). Microprobe analysis indicated that the gangue minerals consist of fine grains hornblende (common gangue minerals) range in composition from magnesio-hastingsite to ferro-hornblende and clinopyroxene ranges in composition from ferrosalite (Wo<sub>50.07</sub> En<sub>13.57</sub> Fs<sub>36.36</sub>), hedenbergite (Wo<sub>49.99</sub> En<sub>7.01</sub> Fs<sub>42.99</sub>), ferrohedenbergite (Wo<sub>32.14</sub> En<sub>5.53</sub> Fs<sub>62.33</sub>) to ferroaugite (Wo<sub>56.26</sub> En<sub>0.04</sub> Fs<sub>43.71</sub>). The iron ore additionally contain grunerite and Andradite (al<sub>3.26</sub> py<sub>0.3</sub> gr<sub>40.17</sub> sp<sub>0.89</sub> uv<sub>0.07</sub> an<sub>55.03</sub>) which means that the ore is associated with both hornfels amphibole-garnet ore skarn.

### 3.1.2. The country rocks

The country rocks represent the lower part of Qandil Group (or Penjween Massif of Jassim et al. 1982) and wedged between the diorite and the much peridotite intrusion. The metamorphosed country rocks show a wide variety in mineral composition. This study proved that the country rocks of the Asnawa iron ores are composed mainly of hornfels with thin layer of carbonate exoskarn (endoskarn of Al-Bidary 2011) and amphibole- garnet ore skarn. According to Al-Bidary (2011) microprobe analysis indicated that the country rocks are mainly composed of clinopyroxene, plagioclase-pyroxene, amphibolite, clinzoeseite, perhinite and chlorite with accessory minerals sphene, sulfides, calcite, quartz, apatite, zircon and magnetite. The latter author added that Clinopyroxene is the most important forming mineral group in the country rocks and consists of ferrosalite, hedenbergite and ferroaugite. It occurs as small aggregate, the composition of ferrosalite is  $Wo_{49.89} En_{16.77} Fs_{33}$ , hedenbergite  $Wo_{46.68} En_{8.7} Fs_{45.2}$  and ferroaugite  $Wo_{41.8} En_{17.53} Fs_{40.83}$ . Plagioclase is fine grained; most grains have lost twin lamella due to metamorphic effect (Nesse, 1986). There are two generations of plagioclase; it is either a primary in the rocks or secondary mineral deposited in fractures by hydrothermal veins to Al-Bidary (2011).

The minerals composition of the plagioclase ranges from albite ( $An_{4.32} Ab_{95.21} Or_{0.46}$ ) to ( $An_{9.17} Ab_{90.33} Or_{0.50}$ ), Andesine composition is  $An_{33.90} Ab_{65.64} Or_{0.45}$ , Labradorite composition is  $An_{60} Ab_{39.28} Or_{0.72}$  to  $An_{64.20} Ab_{35.06} Or_{0.74}$ . Amphibole group in the country rocks composed of Ferro-actinolite and Magnesio-Hastingsite. Ferro- actinolite is found in the country rocks as veins cutting the county rocks or as fine acicular, elongate or fibrous grains parallel to the vein walls. Ferro-actinolite composition is  $K_{0.05} Na_{0.06} Ca_{2.1} Mg_{1.28} Fe^{+2}_{3.56} Fe^{+3}_{0.0} Mn_{0.01} Ti_{0.1} Al_{0.38} Si_{7.68}$ . Magnesio-Hastingsite occurs as aggregates with a schistose texture or as fine-grain with composition of  $K_{0.32} Na_{0.45} Ca_{2.12} Mg_{0.99} Fe^{+2}_{3.08} Fe^{+3}_{0.13} Mn_{0.02} Ti_{0.1} Al_{2.67} Si_{6.0}$ .

## 3.2. Geochemistry

### 3.2.1. Major elements

The obtained major, trace and rare earth elements (REE) data for the Asnawa iron ore and the country rocks are given in (Table 1). Major element geochemistry shows that both Asnawa iron ore and the country rocks are characterized by an extend range of major oxide concentration.  $Fe_2O_3$  is the dominant major oxide in the iron ore which derived from

magnetite ranging between 30.31-70.18% with an average of 63.26%. This concentration increases in the pure iron ore and range between 84.74-93.98%.  $Fe_2O_3$  concentration in the country rocks range between 6.93-24.79% with an average of 15.86%, the main source of  $Fe_2O_3$  in the country rocks came from the amphibole minerals.

### 3.2.2. Geochemistry of REEs

Rare earth elements (REE) geochemical data are obtained for both iron ore and country rocks in Asnawa (Fig. 5). The obtained data have been normalized relative to chondrite values of Sun and McDonough (1989) and the results are given in (Table 2). The residence of REE in metamorphic rocks depends on the minerals present in the rock, the model abundance of those minerals, and the physical and chemical conditions in which those minerals grew (Lipin and McKay 1989).

The REE patterns of a metamorphic rock can be used as evidence of the mineralogy of the source rock, the rock phases altered by the solution and the chemistry of solution (Graf 1977). Implying that the alteration processes and metamorphic fluid (hydrothermal solution) is capable of complexing the REE and removing them from the system (Henderson 1984; Hongo et al. 2007). Accordingly the overall chondrite-normalized REE patterns of the Asnawa iron ore and their country rocks studied display significant REE variability. This indicates that hydrothermal solutions which deposited magnetite are rich with REE and tends to remain in the solution (Henderson 1984).

The REEs in the iron ore rocks have a noticeably negative Eu anomaly due to plagioclase fractionation as well as enrichment in light-REE (LREE) and in heavy REE (HREEs) due to increasing of Fe within magnetization. The country rock display enrichment in the total REEs of 10 x chondrite to 100 x chondrite because the country rocks contain high amount of hornblende deposited from hydrothermal solutions, essentially the REE are hosted in hornblende, whereas  $Ca^{+2}$  in hornblende is replaced by REE (Mason 1952). Generally the country rocks shows enrichment in light-REE and depletion in heavy REE with slight negative Eu-anomaly due to plagioclase fractionation. The Asnawa iron ore and the country rocks REE pattern is coincides strongly with that of the average REE pattern of metasedimentary rocks (Cullers et al. 1997), these clear similarities indicate that they are derived from metasedimentary protoliths.

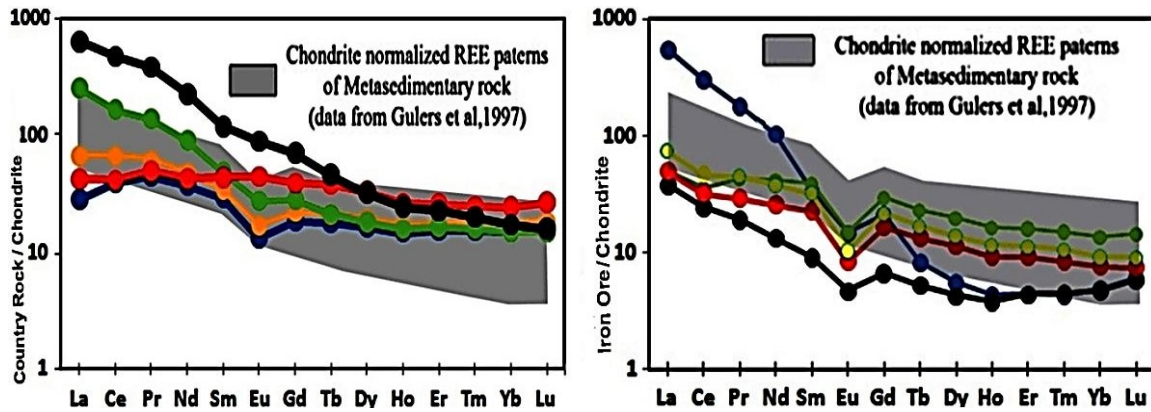


Fig. 5. Chondrite-normalized REE plots for Asnawa country rocks, which is compared to the metasedimentary rock pattern (Data from Cullers et al., 1997).

Table 1: Whole-rock major (wt %) and trace (ppm) element analysis of Asnawa iron ore (R), pure magnetite (RM) and country rock (C).

Oxide wt. %	R1	R2	R3	R4M	R5M	C1	C2	C3	C4	C5
SiO <sub>2</sub>	18.23	13.51	38.1	4.73	9.2	58.06	55.97	49.49	44.7	38.77
TiO <sub>2</sub>	0.127	0.186	0.262	0.174	0.177	0.699	0.799	0.16	0.351	2.334
Al <sub>2</sub> O <sub>3</sub>	3.89	2.22	2.84	1.37	2.3	14.39	15.72	12.49	7.54	12.04
Fe <sub>2</sub> O <sub>3</sub>	70.18	77.25	37.31	91.98	83.74	6.93	7.4	14.19	24.49	22.17
MnO	0.151	0.125	0.257	0.08	0.116	0.096	0.086	0.22	0.297	0.165
MgO	1.16	1.47	3.08	0.28	0.56	2.1	1.99	2.14	2.7	4.24
CaO	6.51	5.61	16.26	1.66	2.97	10.33	9.71	17.05	20.18	15.46
Na <sub>2</sub> O	0.46	0.12	0.41	0.13	0.21	5.54	4.77	1.71	0.2	0.94
K <sub>2</sub> O	0.45	0.12	0.3	0.15	0.21	0.97	1.57	1.13	0.12	1.14
P <sub>2</sub> O <sub>5</sub>	0.09	0.1	0.3	0.02	0.05	0.18	0.14	0.15	0.16	1.27
LOI	1.61	1.37	0.84	1.7	1.40	0.10	0.46	0.40	0.48	1.42
TOTAL	102.86	102.08	99.95	102.27	100.93	99.40	98.63	99.13	101.21	99.95
Trace										
Cr	28	23	32	84	63	60	73	55	62	289
Ni	440	578	435	347	212	78	103	95	1230	100
Co	74	75	108	70	59	19	20	56	84	69
Cu	<10	<10	60	<10	20	20	<10	20	30	90
Zn	99	106	89	80	99	25	30	58	101	88
V	27	97	46	36	33	135	130	103	73	273
Rb	5	4	10	2	2	31	57	30	4	29
Sr	26	23	33	8	13	526	260	344	260	193
Zr	29	26	40	18	30	149	170	123	71	99
Hf	0.8	0.7	1.4	0.4	0.6	3.6	4.3	3.9	2.2	1.9
Th	4.71	1.37	2.66	1.27	1.92	8.62	9.19	8.65	2.55	6.6
U	0.34	0.25	0.36	0.15	0.14	1.97	2.32	1.97	0.99	1.66

### 3.3. Normalized Multi-elements spider diagram

The multi-element variation diagrams (spider diagrams) of Asnawa iron ore and the country rocks are shown in Fig. (6). In the figure the trace elements are arranged in order of decreasing incompatibility from left to right, and normalized to the N-MORB source mantle concentrations of Sun & McDonough

(1989). Bulk-rock N-MORB normalized profiles of iron ore are almost flat in the MREE–HREE region with the flattening of profiles in the Gd–Lu range (5–11) times N-MORB composition). Compared to the country rocks, iron ore has extremely high content of REEs, displaying variable depletions in the moderately incompatible high-field-strength elements (HFSE) (Zr,

Hf, Y) relative to their adjacent. Notable differences in the iron ore spider diagram patterns (Fig. 6) include: (1) Large ion lithophile element (LILE) and LREE values are notably high, with low content of Rb, K, Sr.

The low variations in Rb, K and Pb concentrations and the 'spiky' LILEs indicate interaction of hydrothermal fluids and mobility of these trace elements during magnetite formation. (2) The spider diagrams show a significant negative Ti anomaly for all samples, with relatively flat patterns in the HFSEs, the Ti negative anomaly is due to reduction environment existing

during magnetite formation. The spider diagram patterns for country rocks (Fig. 6) shows, (1) comprehensible enrichment in the LILEs elements indicating their sedimentary protolith (impure limestone of Qulqula Formation metamorphosed to calc-schist and hornfels) with low content of Rb and K; (2) relatively flat patterns in the HFSEs with, (3) negative Ti anomaly due to accessible reduction environment available as indicated by occurrence of dark bands of magnetite in the calc-schist country rock.

Table 2: Present the real REE analysis Normalized whole-rock REE analysis of Asnawa iron ore (R), pure magnetite (RM) and the country rocks (C). Chondrite normalized values from (Sun and McDonough 1989).

REE	R1	R2	R3	R4M	R5M	C1	C2	C3	C4	C5
La	549.63	38.09	49.85	48.99	73.71	27.99	66.46	251.38	42.35	634.85
Ce	301.72	24.701	35.64	31.49	46.58	39.29	66.81	163.95	41.11	470.82
Pr	180.69	19.3	42.53	28.84	44.66	44.55	61.95	135.8	49.38	381.59
Nd	103.89	13.35	41.11	25.64	37.79	37.13	47.52	88.41	41.99	223.25
Sm	33.92	8.97	38.68	22.36	31.74	29.16	34.05	48.13	43.5	118.96
Eu	14.75	4.64	14.82	8.33	10.35	13.08	17.21	27.142	44.28	88.57
Gd	20.95	6.61	29.29	16.42	21.51	18.26	22.07	28.2	39.16	70.19
Tb	8.26	5.23	22.86	13.49	16.8	17.63	20.93	21.21	37.74	45.73
Dy	5.48	4.24	19.4	11.28	13.76	16.15	19.48	18.005	32.92	31.85
Ho	4.31	3.77	16.18	9.17	11.51	14.56	17.08	15.64	26.25	24.1
Er	4.4	4.34	15.92	9.18	11.2	15.1	17.8	16.17	25.99	22.46
Tm	4.29	4.42	14.87	8.34	10.45	15.04	18.09	15.9	24.62	19.83
Yb	4.92	4.67	13.41	7.63	9.107	14.76	17.84	14.83	24.24	17.1
Lu	6.008	5.8	14.07	7.4	9.01	14.97	18.51	14.97	26.66	15.72

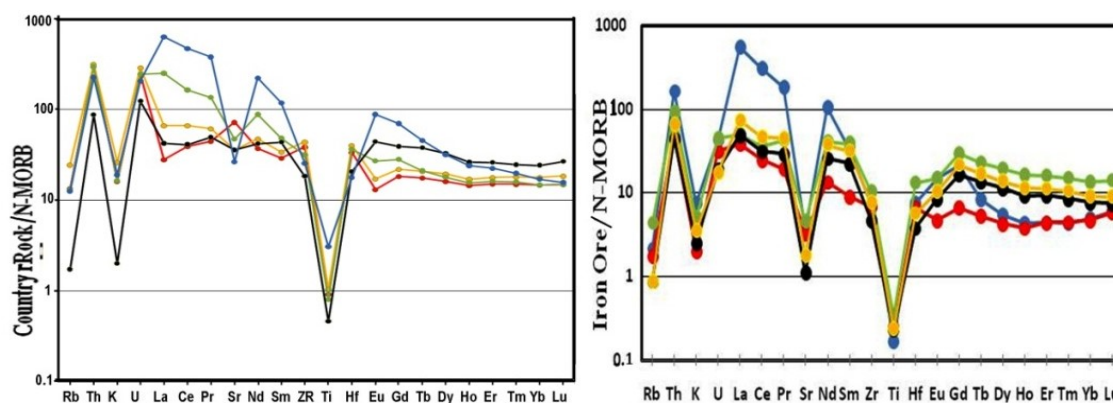


Fig.6. A multi-element spider diagram, normalized against N-MORB of iron ore. Values of normalizing from Sun & McDonough (1989). Elements arranged in order of increasing compatibility (Hofmann 1988).

**3.4. Geochronology**

Two samples of Hornblende (Mg-hastingsite) are separates from Asnawa country rock and iron ore have been dated using  $^{40}\text{Ar}/^{39}\text{Ar}$  method (table 3 and 4). The used instruments was a computer controlled high-sensitivity mass spectrometer type VG-3600 with Tantalum double vacuum resistance furnace for Argon analyses. The samples irradiated for 10 hours at the McMaster nuclear reactor in Canada, and the system is calibrated using the Fish Canyon tuff sanidine standard with an age of 28.2 Ma. Mg-hastingsite in country rock

sample is associated with ferrosalite, plagioclase, clinozoisite and sphene, while in iron ore sample; it is associated with magnetite and ferroaugite. Country rock and iron ore samples yield perfect plateau ages  $37.5 \pm 0.8$  Ma and  $40.8 \pm 0.8$  Ma respectively (Fig.7 and 8). Different ages of the two Mg-hastingsite examples indicate presence of two generation of hornblende in Asnawa and the interrelation between magnesio-hastingsite and magnetite in iron ore rock suggests the contemporaneous formation (mineralization age) of hornblende with magnetite during Eocene time.

Table 3: Argon summaries for hornblende in country rock

T°C	$^{39}\text{Ar}$ (mV)	$^{39}\text{Ar}$ (%)	Age (Ma) $\pm 1\sigma$	$^{37}\text{Ar}/^{39}\text{Ar}$	$^{36}\text{Ar}/^{40}\text{Ar}$	$^{39}\text{Ar}/^{40}\text{Ar}$	% IIC*
750	5.1	1	66.5 $\pm$ 31.49	16.04	0.003275	0.001989	8.51
850	4.3	0.9	22.9 $\pm$ 3.14	16.34	0.002894	0.026291	23.37
950	18.9	3.9	36.6 $\pm$ 1.26	6.81	0.002237	0.038398	6.24
975	55.6	11.6	38.1 $\pm$ .35	5.05	0.000887	0.080459	4.46
1000	121.9	25.5	37.9 $\pm$ .23	4.87	0.000376	0.097386	4.32
1025	37.2	7.8	37 $\pm$ .36	5.19	0.000864	0.083597	4.71
1050	28.5	5.9	36.1 $\pm$ .38	5.36	0.000955	0.082479	4.97
1075	25.4	5.3	37 $\pm$ .37	5.64	0.000789	0.086068	5.12
1100	16.7	3.5	34.8 $\pm$ .4	6.03	0.001016	0.083422	5.79
1125	12.8	2.6	34.1 $\pm$ .4	6.57	0.001095	0.082383	6.43
1150	16.3	3.4	36.8 $\pm$ .38	6.34	0.000796	0.086309	5.79
1175	5.9	1.2	31.9 $\pm$ .85	7.34	0.00168	0.06566	7.67
1200	4.6	0.9	33.8 $\pm$ 3.38	8.11	0.002894	0.017814	8.02
1300	30.5	6.4	37.2 $\pm$ .37	7.48	0.00087	0.082901	6.75

Total Gas Age =  $37.5 \pm 8$  Ma,  $J = .002329 \pm 2.329\text{E-}05$ , \*% IIC - Interfering isotopes correction

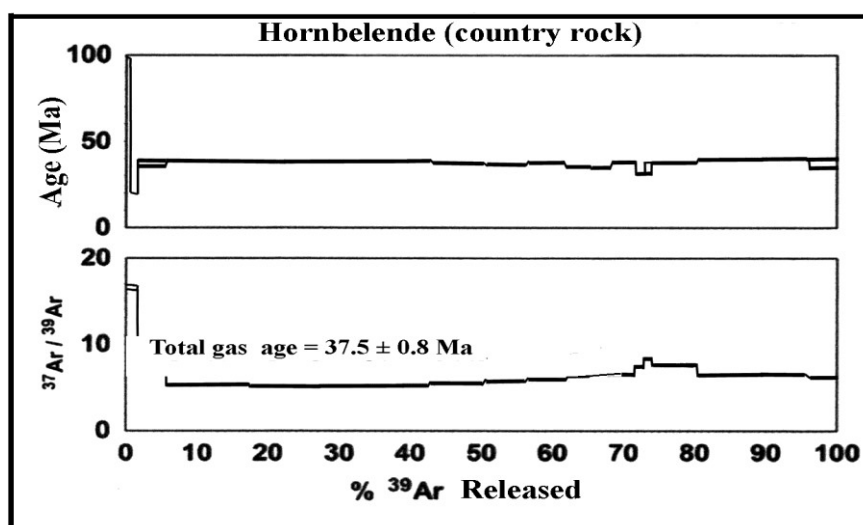


Fig.7. Plateau age of Asnawa country rock by released  $\text{Ar}^{39}$  from hornblende



Table 4. Argon summaries for hornblende in Iron ore body

T <sub>o</sub> C	<sup>39</sup> Ar(mV)	<sup>39</sup> Ar(%)	Age(Ma)±1σ	<sup>37</sup> Ar/ <sup>39</sup> Ar	<sup>36</sup> Ar/ <sup>40</sup> Ar	<sup>39</sup> Ar/ <sup>40</sup> Ar	% IIC*
750	3.4	0.3	214 ± 57	8.79	0.003199	0.00101	1.79
850	9.1	0.8	50.1 ± 2.2	7.24	0.002415	0.023682	4.97
950	251.9	22.7	39.3 ± 0.2	4.63	0.000393	0.093351	3.97
975	364.5	32.9	38.6 ± 0.2	4.63	0.000159	0.102641	4.04
1000	70.1	6.3	39.2 ± 0.3	4.66	0.000536	0.08926	4.02
1025	14.5	1.3	47.6 ± 0.7	4.98	0.001414	0.050711	3.58
1050	25.2	2.2	50.1 ± 0.5	4.88	0.000894	0.06169	3.35
1075	41.5	3.7	47.4 ± 0.3	4.85	0.000531	0.073796	3.50
1100	73.7	6.6	43.9 ± 0.3	5.02	0.00042	0.082821	3.89
1125	96.7	8.7	42.8 ± 0.2	5.33	0.000219	0.090664	4.23
1150	60.4	5.4	38.6 ± 0.2	5.3	0.000362	0.096052	4.62
1200	23.2	2.1	38.3 ± 0.4	5	0.000984	0.076964	4.39
1300	26.9	2.4	36.9 ± 0.8	4.89	0.00183	0.051706	4.45
1400	4.0	0.3	30.3 ± 7	4.97	0.003153	0.009389	5.45
1440	1.5	0.1	0.7 ± 23	4.82	0.003382	0.002929	192.53

Total Gas Age = 37.5 ± 8 Ma, J = .002329 ± 2.329E-05, \*% IIC - Interfering isotopes correction

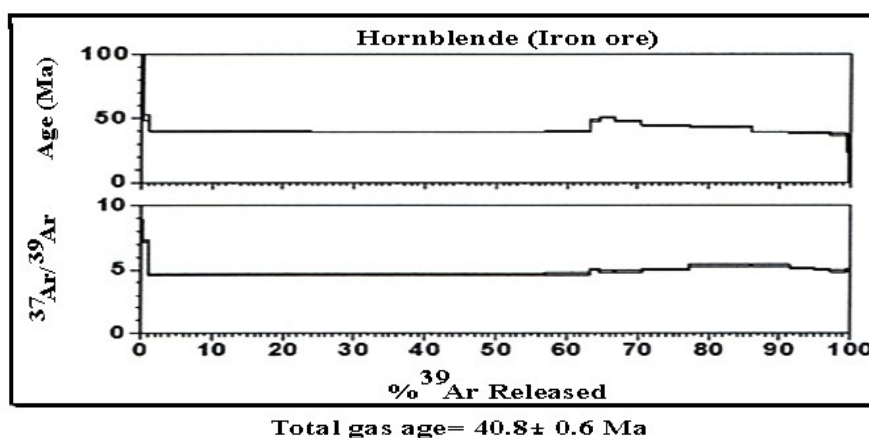


Fig. 8. Plateau age of Asnawa Iron ore body by released Ar<sup>39</sup> from hornblende

### 3.5. Thermo-barometry

Mineralogical study of the Asnawa iron ore reveals that the amphibole and plagioclase are the major constituents of the Asnawa iron ore. Amphibolite minerals exist in both iron ore body and the country rock, it occurs as gangue and main mineral constituent respectively. The amphibole (hornblende) minerals within the iron ore body range in composition from magnesio-hastingsite to ferro-hornblende, while the amphibole mineral in the country rock is composed of Ferro-actinolite and Magnesio-Hastingsite.

Based on amphibole thermobarometry of Ernst and Liu (1998), amphiboles of the iron ore represent high PT metamorphic conditions (Fig. 9). The estimated metamorphic temperature of the iron ore range between 550-650 °C (Hornblende Hornfels facies), while the temperature of the country rocks range from 420-540 °C (Albite-Epidote Hornfels to Hornblende Hornfels facies).

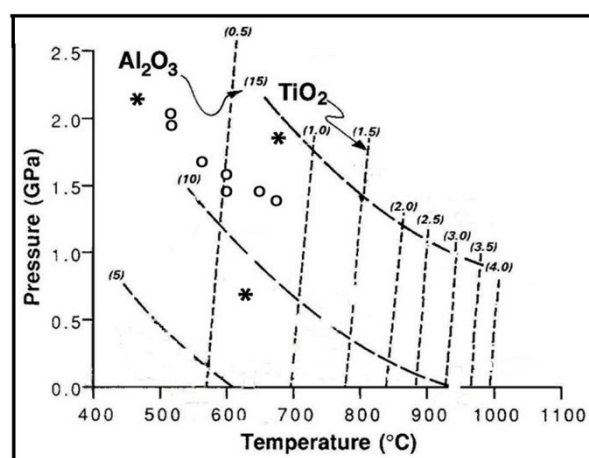


Fig. 9. Compositions of amphiboles in Asnawa iron ore (o) and Asnawa county rocks (\*) plotted on an isopleth of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> diagram of calcic amphibole (after Ernst and Liu 1998).

## 4. Discussion

### 4.1. Paragenesis of Asnawa Iron Ore

The paragenesis of the of the Asnawa Iron Ore is depending on the field and lab evidence. The paragenesis elements include the deposition and age of the parent rocks in additions to burial and metamorphism of these rocks to calc-silicate rocks. The metamorphic calc-silicate rocks are suffered from second phase of metamorphism by intrusion of iron rich hydrothermal solution.

#### 4.1.1. Field evidences

In the area, there are two types of metamorphic rocks (both are called calc-silicate rocks in this study) that are related to iron ore; the first one is relatively thin (10-30cm thick) layer (or vein) of skarn rocks which exist at the northwestern boundary of the iron ore. This skarn is assigned as carbonatite (magmatic carbonate rocks) by Yara (2014). The second is banded hornfels previous schist of McCarthy (1956), Pishdari (1983); Aswad and Pshdari (1985) and orthogneiss of Yara (2014). The hornfels is covering both the first one and iron ore from all sides to the distance of three hundred meters between diorite at southeast and peridotite at the south and southwest. Outside this distance, the hornfels rocks changes to calc-silicate marble, especially inside and around Penjween town. In the present study and according to the field evidence and Karim (2004) it is proved that the above three rock have sedimentary parenthood (protolith). This proof is important for introduction of new explanation of the association of iron ore, different metamorphic and sedimentary rocks and effect of metamorphism on them.

The closest sedimentary unit to the iron ore calc-silicate rocks is Merga Red Bed (Miocene) and the Qulqula Radiolarian Formation, the outcrop of which is located about 5 kms to the south and southwest of the studied area near Kani Manga village (Fig. 1). The country rock around the iron ore (now metamorphosed to hornfels) is very similar to the lithology and bedding pattern of Qulqula Radiolarian Formation which was studied in detail by Baziany (2014) and Karim et al. (2009). If the distance of the five kilometers is not covered by the peridotite and later series, it is possible to trace laterally the formation into calc-silicate marble. According to the latter two authors, the latter formation contain both impure limestone and calcareous shale, therefore the parent rock of the calc-silicate rock is most possibly the Qulqula Radiolarian Formation. The hornfels has clear banded and foliated texture (or structure) which originally inherited from impure or banded limestone which was regionally metamorphosed. Karim (2004) found layered (bedded) metamorphic rocks that were very similar to the bedded limestone and cherts of Qulqula formation in thickness, stacking pattern and color. Therefore he considered the formation as the parent rock of the marbles (present calc-silicate rocks) in Penjween area.

According to Karim (2003), the Qulqula Radiolarian Formation is deposited in the trench of the Neo-Tethys and finally deformed and accumulated as accretionary prism during colliding of Arabian and Iranian plates. The pressure and temperature of the colliding metamorphosed the rocks of the accretionary prism regionally. During the metamorphism the calc-silicate marble obtained the clear foliation which appears as black and white bands (similar to lamination in sedimentary rocks). These bands can observe on the outcrop and quarries of calc-silicate marble which used as decorative stone in the Iraqi Kurdistan, including studied area, and studied by Karim (2004).

#### 4.1.2. Hornfels rocks

Pashdari (1983) and Aswad and Pshdari (1985) assumed that the iron ore exist inside the skarn and calc-silicate rocks as contact aureole of the Asinawa iron ore while the Al-Bidary (2011) concluded that the ore has a contact with gabbro. While Yara (2014) has discussed that the iron ore surrounded by carbonatite and orthogneiss rocks.

In the present study, a new rock (hornfels) is introduced as a main country rock of the Asnawa. The hornfels consists of banded (finely layered) and coherent and stiff rocks which are sound when strike with hammer. These rocks consist of light and dark color bands of thickness ranging from less of millimeter to few centimeters (Fig. 10 and 11).

The dark bands of the hornfels consist of amphibole and pyroxene minerals while the light ones consist of plagioclase minerals (albite, oligoclase and andesine). The bands are originally consisted of the pure and impure calcitic limestone bands of calc-silicate rocks. The origin of these bands are studied in marbles in detail by Karim (2004) in the area around Penjween. The intrusion of a hot iron solution into the calc-silicate marble transformed the rocks to contact metamorphic rocks (hornfels). By this process the pure calcite bands (lamina) are changed to plagioclase and impure ones are changed to amphibole and pyroxene minerals due to presence of silicate minerals. It is clear that the original texture and structure of the calc-silicate marble not and only the mineralogy is changed by heat and solutions (Fig. 10 and 11). The hornfels can be called the banded hornfels due to the freezing of original texture and structure of the parent metamorphic rocks. The evidence of this assumption is the finding of sanidine inside the iron ore by Al-Bidary (2010) (Fig.12 B, C and D). This mineral is envisaged as index mineral of sanidine hornfels facies of high temperature contact metamorphism. Other evidence is the texture of the country rock which is mostly granobalstic (Fig.12A). Jassim et al (1982) and Jassim and Goff (2006) had mentioned occurrence of hornfels in Bulfat area about 80 kms to the northwest of the studied area.

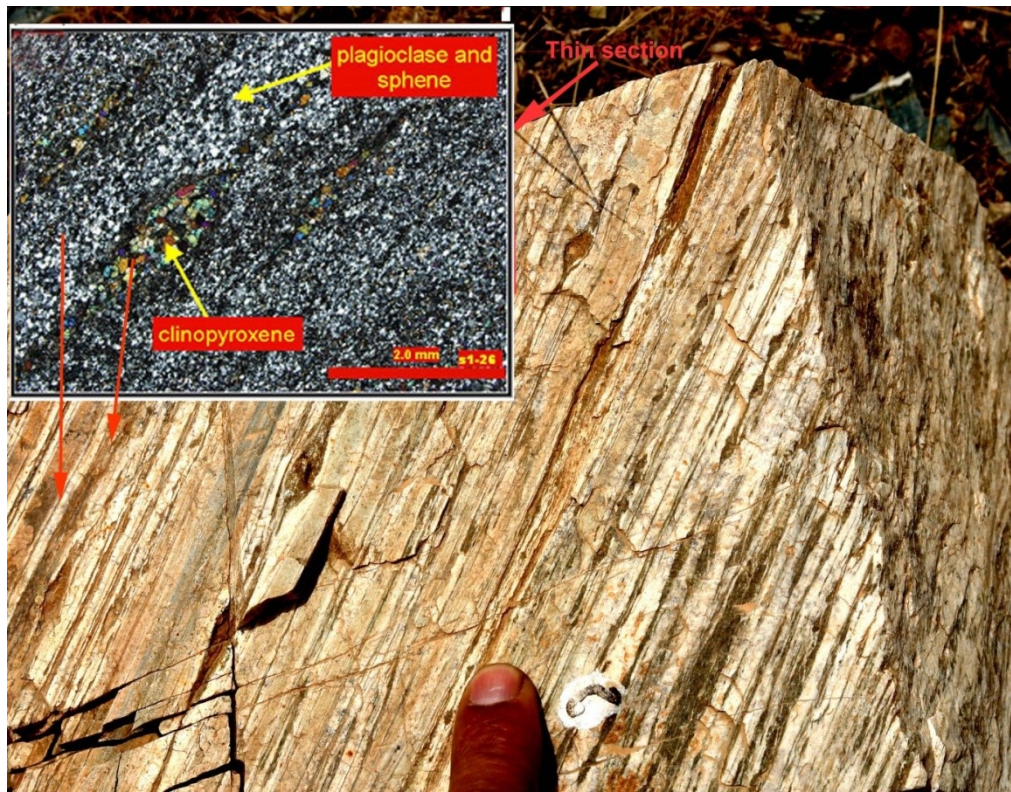


Fig. 10. a) Hand specimen of a banded hornfels of the country rock of the iron ore, the white and dark bands consist of pyroxene (with amphibole) and plagioclase respectively, b) Thin section of a part of hand specimen.

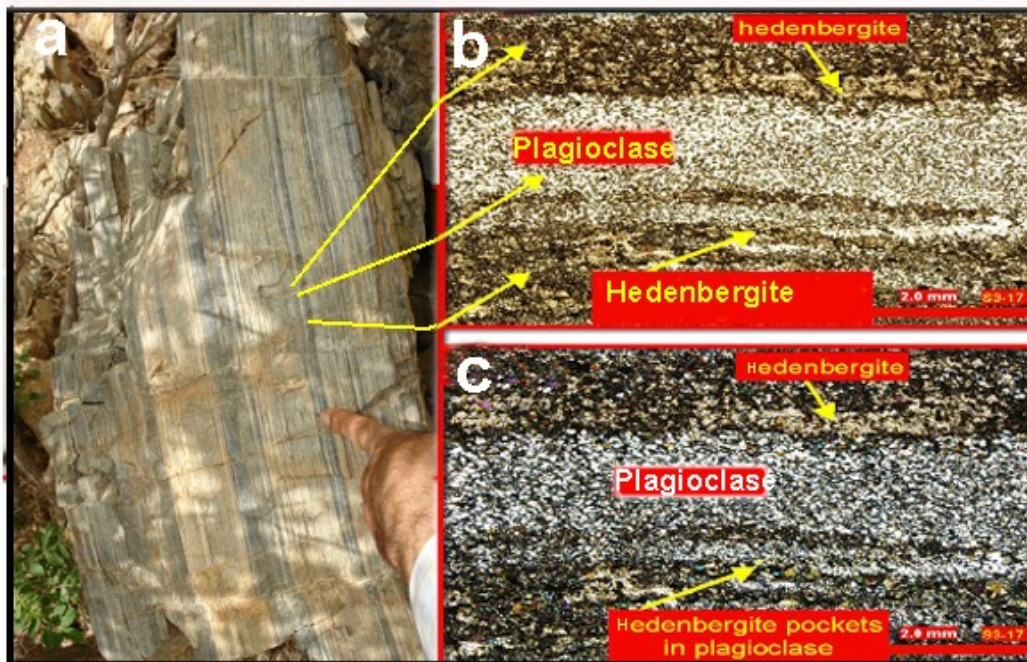


Fig.11. a) Hand specimen of hornfels shows preserved parallel white and gray banding (lamina). b) Thin section of the same sample showing alternation of hedenbergite rich bands and plagioclase ones. PPL, S3, sample no.17. c) Same thin section under XPL.

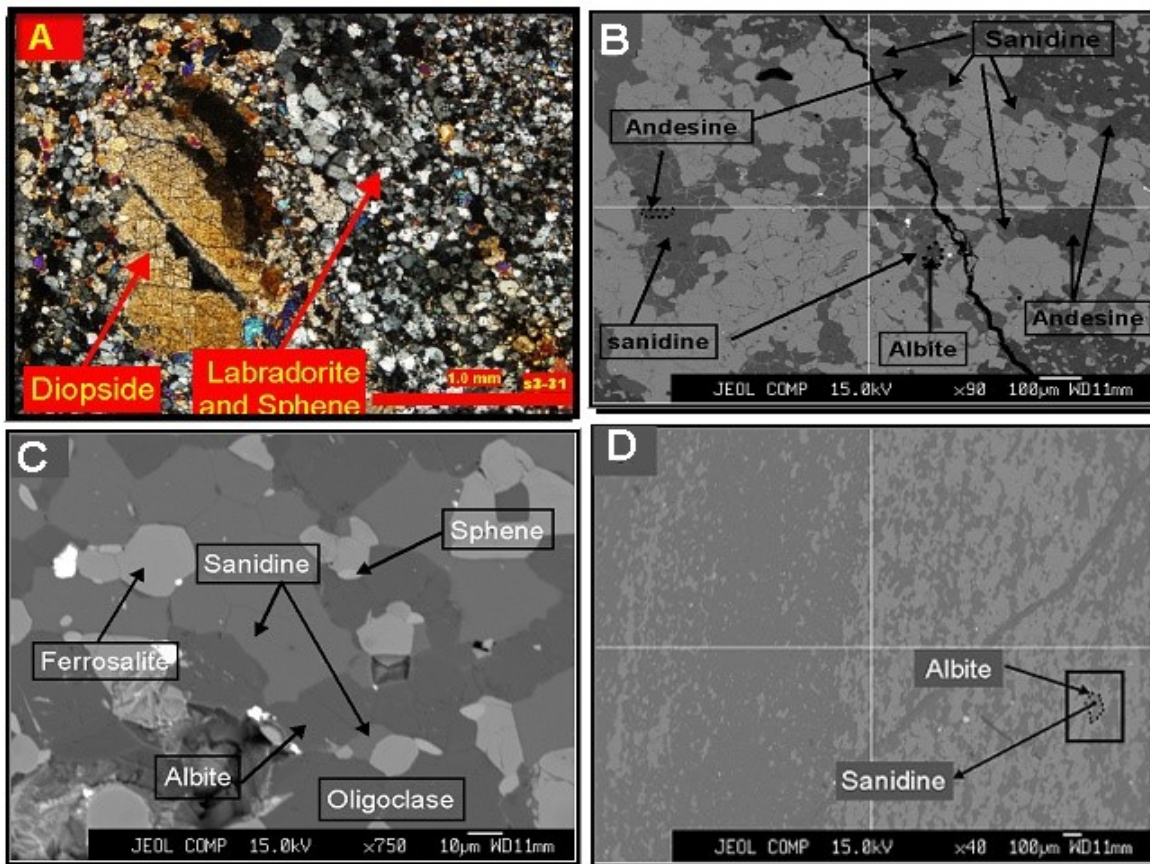


Fig. 12. The different features of the country rocks (hornfels), A) Granoblastic texture of the hornfels shows enlarged plagioclase rich and diopside rich bands. B, C and D) Sanidine in the country rock which indicate hornfels facies of metamorphisms.

The properties of mentioned hornfels are similar to that of the present study such as fineness of grains, spotty appearance with dark and light parts and association with diorite body. McCarthy (1956) considered the present hornfels as siliceous schist which regionally metamorphosed between both igneous intrusions. He added that the parent rock of the schist was sedimentary rock of Qandil Group. In Iran, East Azarbaijan, NW Iran, Mollai et al. (2014) studied geology and geochemistry of skarn deposits in the northern part of Ahar batholith. The deposit is associated nearly with similar mineral assemblage, replacement and facies of the present study. They concluded that a limestone was thermally metamorphosed to hornfels in the range of 698-754 °C.

#### 4.1.2. Carbonatite versus skarn

Yara (2014) has assumed that the thin skarn deposit at the northwestern boundary is carbonatite rocks (Fig.13). His assumption is based on several points: 1) the presence of apatite, sanidine, clinopyroxene and igneous zircon, 2) calcite inclusion within clinopyroxene and sanidine, 3) the geological setting of the carbonatite as lenses within orthogneiss, 4) the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the rock (0.7069). He further added that this ratio suggests that the rock was mantle-

derived and represents a carbonatite rather than limestone. Its intrusive age is determined by the zircon evaporation method; its weighted mean age yielded  $310 \pm 13$  Ma.

The present study does not aid presence of carbonatite in the area due to the five below facts. The first one is that Al-Bidary (2011) found sanidine inside the iron ore and in the country rocks (Fig. 12 B, C and D). The second is presence of laminations in the exposed carbonatite (skarn of present study). These laminations are inherited from the sedimentary protolith (Fig.14A and 15). The third one is occurrence of clear bedding of the country rock around iron ore (Fig.12B and 13). These beds belong to Qulqula Radiolarian Formation and now exists as hornfels.

The fourth one is that the claimed orthogneiss by Yara (2014) is proved in present study that it is hornfels which metamorphosed from calcislate marble. Therefore, the presence of carbonate in it is normal. The fifth one is the fact that metamorphic rock can contain reworked Zircon of igneous origin. The calculated age of 310 million years (Carboniferous) may be belong to the age of crystallization of the igneous body from which the zircon grain inflexed into Qulqula Radiolarian Formation after erosion.

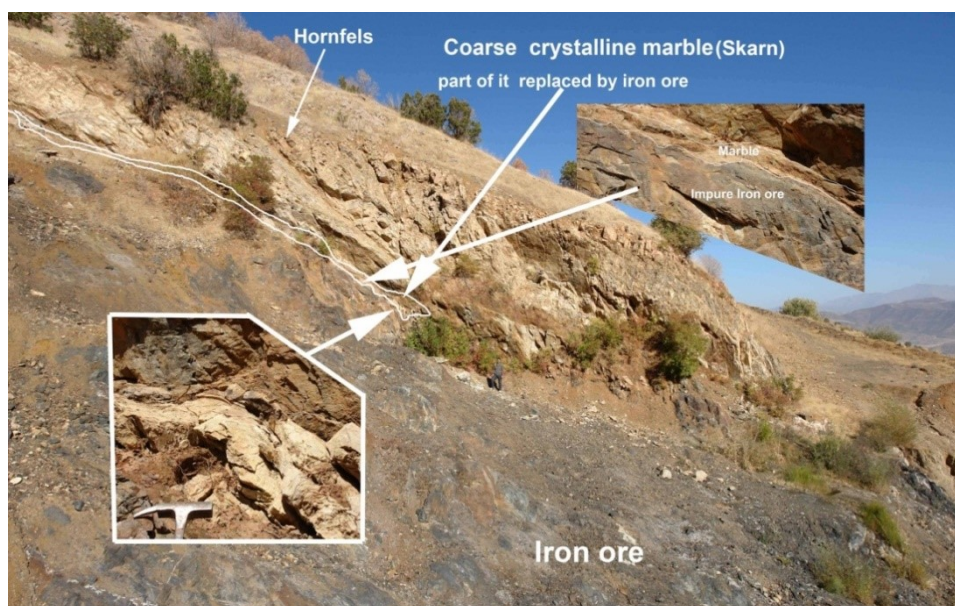


Fig. 13. The main quarry of the iron ore which surrounded by skarn and hornfels. The skarn is assumed as carbonatite by Yara (2014).



Fig.14. A) Sample of the carbonatite of Yara (2014) shows laminations of possible sedimentary precursor, B) Sedimentary bedding around iron ore at the distant of 150 to its northwest, the beds now metamorphosed to hornfels (consisted of plagioclase rich and amphibole rich bands).

## 5. History and processes of paragenesis

The history and processes of paragenesis of the iron ore is shown in the figure (16) and described in the below points.

1-The Qulqula Radiolarian Formation (marls, bedded charts and limestone) was deposited in the trench of the Neo-Tethys basin during Jurassic and Early Cretaceous (Fig.16 a).

2-The formation had deformed to an accretionary prism in between the Arabian and Iranian plates during their collision in Late Cretaceous (Fig.16b) with concurrent obduction of ophiolite (Karim, 2003).

3- The part of the formation that is located inside Sanandij-Sirjan Zone (Penjween area or Suture zone) was regionally metamorphosed and transformed to

calc-silicate marble (Fig.16 c) while that part of the formation that is located at 4 km to the south (inside thrust Zone) remained as highly deformed sedimentary rock (Fig.16a).

4- The basic igneous bodies were intruded into calc-silicate marble during Eocene and this latter rock was re-metamorphism to hornfels (Fig.16c) while the pure calcitic marble changed to exoskarn.

5-Iron-bearing magmatic solution separated from a possible deep seated igneous body. The iron ions had partially replaced calc-silicate which was transformed to Iron-ore (Fig.16d).

6- The studied area had uplifted and the iron ore exposed due to erosion of cover rocks during Pliocene and Quaternary.



Fig.15. The country roc at the distance of 200 meters from iron ore showing clear bedding of parent rock which was metamorphosed and now can be seen as hornfels

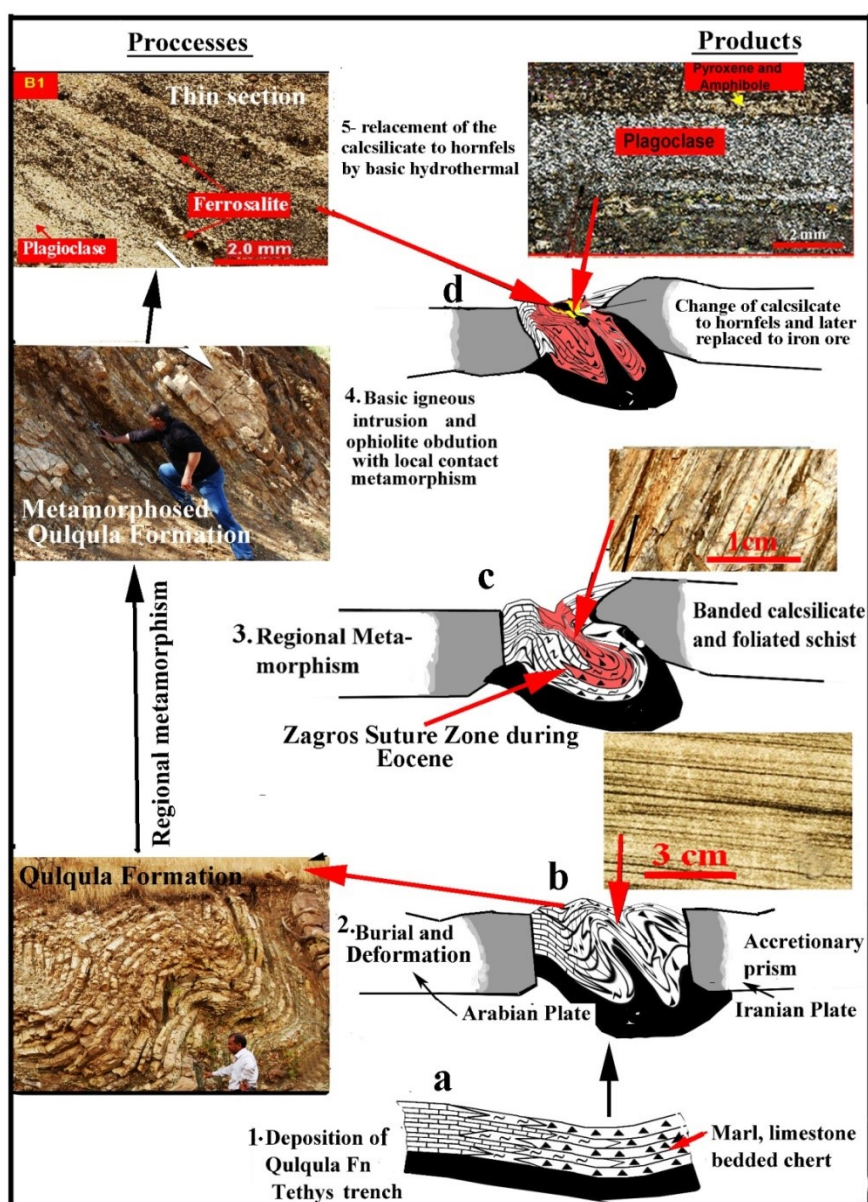


Fig. 16. Graphical model (not to scale) for paragenesis of Asinawa iron ore which evidenced by field and thin section photos.

## 6. Conclusion

1-The overall chondrite-normalized REE patterns and multi-element variation diagrams of Asnawa iron ore and the country rocks shows that the protolith of the country rock was sedimentary impure limestone which is metamorphosed to calc-schist.

2- The sedimentary parent rock of the iron ore and their country rocks was Early Cretaceous Radiolarite (Qulqula Radiolarian Formation) which regionally metamorphosed to calc-silicated schist and finally to thermally changed to hornfels.

3- The metamorphic facies of the country rock is hornblende hornfels with localized and minor occurrence of pyroxenite and sandine facies.

4- The igneous intrusions and contact metamorphism were occurred during Eocene.

5- The study does not aid the presence of previously mentioned carbonatite.

## References

- Al-Bidary M (2011) Mineralogy and Geochemistry of Asnawa iron deposit in Penjwen Area, NE-Iraq. Ph D Thesis, University of Baghdad, 113 p.,
- Aswad K, Pshdari M (1985) Geology, Geochemistry and Genesis of Iron ore Skarn at Asnawa, Penjwen, NE Iraq, *Journal of the Geological Society of Iraq* 18:231-265.
- Baziany MMQ (2014) Depositional Systems and Sedimentary Basin Analysis of the Qulqula Radiolarian Formation of the Zagros Suture Zone, Sulaimani Area, Iraqi Kurdistan Region. PhD thesis, University of Sulaimani, 200p.
- Cullers RL, Bock B, Guidotti C (1997) Elemental distributions and neodymium isotopic compositions of Silurian metasediments, western Maine, USA: redistribution of the rare earth elements, *Geochimica et cosmochimica acta* 61:1847-1861.
- Ernst W, Liu J (1998) Experimental phase-equilibrium study of Al-and Ti-contents of calcic amphibole in MORB -a semiquantitative thermobarometer, *American Mineralogist* 83:952-969.
- Graf JL (1977) Rare earth elements as hydrothermal tracers during the formation of massive sulfide deposits in volcanic rocks, *Economic Geology* 72:527-548.
- Henderson P (1984) General geochemical properties and abundances of the rare earth elements, *Rare earth element geochemistry* 2:339p.
- Hofmann AW (1988) Chemical differentiation of the Earth: the relationship between mantle, continental crust, and oceanic crust, *Earth and Planetary Science Letters* 90:297-314.
- Hongo Y, Obata H, Gamo T, Nakaseama M, Ishibashi J, Konno U, Saegusa S, Ohkubo S, Tsunogai U (2007) Rare Earth Elements in the hydrothermal system at Okinawa Trough back-arc basin, *Geochemical Journal* 41:1-15.
- Jassim S, Buda G, Neuzilova M, Suk M (1982) Metamorphic development of the Iraqi Zagros ophiolite zone, *Krystalinikum* 16:21-40.
- Jassim S, Goff J (2006) Geology of Iraq. Dolin, Prague and Moravian Museum, Brno:341 pp.
- Karim K (2003) A conglomerate bed as a possible lower boundary of Qulqula Formation, from Chuarta-Said Sadiq area, NE-Iraq, *Kurdistan Academician Journal (KAJ)* 2 (A):45-64.
- Karim K (2004) Origin of structures and textures of some Kurdistan marbles as inferred from sedimentary ancestor structures, *NE-Iraq, (JSZ) Journal of Zankoy Sulaimani* 7:69-86.
- Karim K, Habid H, Raza S (2009) Lithology of the Lower part of Qulqula Radiolarian Formation (Early Cretaceous) Kurdistan Region, NE-Iraq, *Iraqi Bulletin of Geology and Mining* 5 (1):9-23.
- Lipin BR, McKay GA (1989) Geochemistry and mineralogy of rare earth elements, *Reviews in Mineralogy* 21:23-40
- Mason B (1952) Principles of geochemistry, *Soil Science* 74:262.
- McCarthy M (1965) Geology of Penjwin area, unpublished report, State Company of Geological Survey and mining, Baghdad-Iraq, 69 p.
- Mollai H, Pe-Piper G, Dabiri R (2014) Genetic relationships between skarn ore deposits and magmatic activity in the Ahar region, Western Alborz, NW Iran, *Geologica Carpathica* 65:209-227.
- Pshdari M (1983) Mineralogy and geochemistry of contact rocks occurring around Hero and Asnawa, NE-Iraq. Unpub. M. Sc. Thesis, Mosul University. 139p.
- Sun SS, McDonough WF (1989) Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes, *Geological Society, London, Special Publications* 42:313-345.
- Teretenko N, Khadikov B (1961) Report on prospecting exploration of the Asnawa iron ore deposit and Mishau iron ore occurrence, *Manuscript report*.
- Yara IOM (2014) Do Asnawa Rocks (Kurdistan, Iraq) Represent Subcontinental Mantle?: New Insight by Petrology, Mineral Chemistry, Geochemistry and Isotopes, PhD thesis. Faculty of Geosciences, Geo-Engineering and Mining of the Technische Universität Bergakademie Freiberg, Germany. 150p.