

## **Hydrothermal-metasomatic origin in the Qatruyeh iron occurrences, Sanandaj-Sirjan zone, SW Iran: Evidence from mineralogical textures, trace elements and fluid inclusions**

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### **Abstract**

*The Qatruyeh iron deposits are located in the eastern edge of the NW-SE trending Sanandaj-Sirjan metamorphic zone of southwestern Iran and are hosted by a Late Proterozoic to Early Paleozoic sequence dominated by metamorphosed carbonate rocks. The magnetite ores occur as massive to layered bodies, with lesser amounts within disseminated magnetite-hematite-bearing veins. Field and textural observations, along with geochemical data in high-grade massive magnetite ores suggest an amagmatic origin. Geochemical analyses of the high field strength elements (HFSEs), large ion lithophile elements (LILEs), and REEs indicate that mineralization within the low-grade layered magnetite ores was related to magmatic process accompanied by Na-Ca alteration. Subsequent to the formation, low-temperature hydrothermal activity produced hematite ores with associated propylitic-sericitic alteration. The metacarbonate host rocks are LILEs-depleted and HFSEs-enriched due to metasomatic alteration. REEs were relatively immobile during the alterations and can be used as indicators in different ores genesis. Data from fluid inclusions suggest that low grade magnetite ores were deposited at temperatures between 180 and 435 °C from fluids with salinities between 3.5 and 15 wt. % NaCl equiv. at pressures below 280 bars. Cooling and increasing of pH, effervescence and fluid mixing may play an important role in the formation of the low grade magnetite ores.*

**Key words:** *Iron deposits, Sanandaj-Sirjan metamorphic zone, hydrothermal-metasomatic, fluid inclusions, Iran.*

### **1. Introduction**

The last decade has seen major progress in our understanding about the origin of iron ore deposits worldwide. The majority of interpretations center on the iron oxide deposits either having formed by magmatic liquid immiscibility [1] or by hydrothermal alteration and replacement [2]. The hydrothermal iron deposits are commercially far less important as global source of iron than banded iron formations and igneous iron deposits, but many countries without these deposits depend upon them. Genetic models for hydrothermal Fe-oxide deposits associated with hybrid magmatic to non-magmatic fluids, which locally mix at the trap site suggest that metamorphic processes or a primitive felsic to intermediate intrusive could be regarded as source of the majority of hydrothermal fluids and metals [3,4]. Therefore, metasomatic iron-rich fluid regimes associated with magmatism or metamorphism, or both. In spite of the existence of the important hydrothermal iron occurrences in Qatruyeh area, there are a few reports on the ores with no exploitation activities. The present paper presents detailed field observations, mineralogical alteration assemblages, textural relationships, fluid inclusions and geochemical data on ore bodies, the associated dolomitic-marble host and

plutonic rocks at Qatruyeh iron ores, Iran, in order to reveal a genetic model for the occurrences in the studied area.

## **2. Materials and Methods**

### **2-1 Geological Setting and Orebodies geology**

The Qatruyeh area is located about 50 km NE of Neyriz, and lies within the Sanandaj-Sirjan zone in SW of Iran (Fig.1). [5] Classified five rock groups (orthogneiss, amphibolite, alternation of chlorite-schist and dolomitic-marble, micaschist-quartzite and limestone) in Qatruyeh area, base to top, from low- to high-grade metamorphic rocks, unconformably overlain by upper Triassic turbidite rocks and basalt which is still poorly known [5]. An intrusive (Chah Anjir intrusive rocks) ranging from dioritic to monzodioritic in composition and about 1 km in diameter is located in the south of the area showing chilled margin. All orebodies occur within the dolomitic-marble and chlorite-schist rocks of the early Paleozoic. The orebodies can be divided into massive and layered magnetite ores with minor hematite. The massive magnetite ores are most often horizontal to sub-horizontal in contact with micaschists and dolomitic-marbles. They are often in very small sizes which their occurrences never exceed 5 m<sup>2</sup>. Whereas, the layered magnetite ores, from a few cm to several meters wide ( $\leq 10$  m), are found throughout the area interbedded with the stratified metacarbonate rocks. These host rocks were strongly affected by sodic-calcic alteration. The sodic-calcic alteration zones are spatially associated with layered magnetite bodies that appear to have replaced marbles, dolomitic-marbles, and chlorite-schist rocks. Minor hematite occurrences found in the upper parts of the brecciated metacarbonates. Hematite also appears in the mylonitized metacarbonate rocks, which display propylitic alteration near the fault contacts.

### **2-2 Petrography and alteration assemblages**

Microscopic observations on ore body host rocks indicate that replacement textures due to alteration are dominant. These include widening of a fracture filling irregular mass where a fracture crosses a chemically reactive rock, irregular or vermicular intergrowths of hematite and calcite-dolomite, islands of non-replaced host rock, rims of one mineral penetrating another along its crystallographic direction, non-matching walls or borders of a fracture, cusp and caries textures. Microscopic observations and X-ray diffraction patterns on ore samples and metacarbonates have led to the recognition of two main alteration stages in the layered magnetite- and hematite-bearing ores. The first stage includes Na-Ca metasomatism (actinolite+albite+titanite+tourmaline+paragonite+epidote+siderite+calcite+quartz) which is characteristic of dolomitic-marble host rocks (Fig. 2a). Layered magnetite ores replaced dolomitic-marble and the calc-silicate minerals that are typical of skarns are virtually absent from the ore zones. The second stage of alteration is shown by hematitization in brecciated metacarbonate (Fig. 2b). Hydrothermal activity produced a specific alteration around hematite ores with a more regionally developed propylitic-sericitic zone. The alteration that is associated with oxidizing fluids often results in the formation of minerals with a high Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio and, in particular, hematite with associated sericite +quartz +epidote +chlorite ±magnetite [6].

## 2-3 Sampling and Analyses

Analyses for major and trace elements were carried out on representative samples using inductively coupled plasma optical emission spectroscopy (ICP-OES) at geological survey of Iran (22 ore samples), and using standard wet chemical analysis by flame atomic absorption spectrophotometry (FAAS) at the department of earth sciences, Shiraz university (5 fresh marbles, 11 altered marbles and 12 diorites). Rare earth elements (REEs) were analyzed by inductively-coupled plasma mass spectrometry (ICP-MS) at ALS Chemex Analytical Services, Canada (4 diorites, 22 ore samples).

## 3. Results and Discussion

### 3-1 Geochemistry of Chah Anjir Intrusive Rocks

The Chah Anjir intrusive rocks can be classified as diorite to monzodiorite, within the calc-alkaline to tholeiitic fields (Fig. 3a). According to  $\text{SiO}_2\text{--Fe}_2\text{O}_3/\text{FeO}$  diagram [7], the Qatruyeh plutonic rocks are considered I-type magnetite series granitoids (Fig. 3b). On this basis, the intermediate intrusions would be considered as a potential source of mineralizing components for the iron ore deposits [7]. REEs contents were normalized to chondrites using the values of Wakita et al. (1971). Enrichment coefficient of La ( $(\text{La}/\text{Sm})_{\text{CN}}$ ), La ( $(\text{La}/\text{Lu})_{\text{CN}}$ ), Gd ( $(\text{Gd}/\text{Lu})_{\text{CN}}$ ) and  $[\text{Eu}]/[\text{Eu}^*]$  as Eu anomaly, were examined. The results indicate that the Chah Anjir intrusive rocks were enriched in light rare earth elements (LREEs) compared to heavy rare earth elements (HREEs) (Fig. 3c).

### 3-2 Geochemistry of Iron Ores

The high-grade magnetite ores typically have high contents of  $\text{TiO}_2$  (0.09 to 1.08 wt. %), whereas the low-grade ores have higher contents of  $\text{Na}_2\text{O}+\text{K}_2\text{O}$  (mean 1.08 wt. %) and CaO (mean 3.8 wt. %). According to major oxide analyses of magnetite, the high  $\text{Na}_2\text{O}$  content in magnetites called alkali iron effect, which kept iron in solution at temperatures significantly lower than the melting point of magnetite at rather shallow depth. The REE patterns for magnetites, as well as their geochemical character, show a clear difference between the high-grade and low-grade ores (Fig. 3c). The uniformity of the layered magnetite ores and the REE patterns of the magmatic rocks are consistent with our interpretation of the geology, in which the layered magnetites were formed from magmatic derived hydrothermal fluids. On the contrary, all the different forms of massive magnetite ores in REE distribution patterns indicate that these ores formed at dissimilar times and by different processes (e.g. dehydration and decarbonation reactions during prograde metamorphism and derived metamorphic waters from this process). Lanthanum/gadolinium (La/Gd), plotted against  $\text{Eu}/\text{Eu}^*$  (Fig. 3d) for Qatruyeh iron ores indicate that layered magnetite ores fall in a field of deuteric-metasomatic deposits [8].

### 3-3 Geochemistry of Metacarbonate Host Rocks

High MnO and  $\text{Fe}_2\text{O}_3$  values in altered dolomitic-marbles indicate that Fe and Mn replace Mg in dolomite lattice. In order to evaluate the compositional changes during hydrothermal alteration, the concentrations of elements of interest are compared to those of immobile elements such as Zirconium. In the case of chemically incompatible elements, the regression lines of REEs and HFSEs which are considered to be immobile with each other in the Qatruyeh altered dolomitic-marbles (Figs. 4 a-d). The REEs are less well correlated with the HFSEs and the regression lines shift from the origin, which suggests that the REEs were somewhat mobile during alteration. LILEs (Ba, Sr, Rb and Cs) are more mobile relative to Zr during hydrothermal alteration as shown by their poor correlations in Figures 4 e-f.

### 3-4 Fluid Inclusions

A total of 10 double polished sections, representative of quartz types encountered at Qatruyeh. Based upon their phase content and variable degrees of filling, four types of inclusion are present in samples (Figs, 5 a-d): (1) Two-phase liquid +vapor (type A), (2) three-phase vapor +liquid (L<sub>1</sub>) + CO<sub>2</sub> liquid (L<sub>2</sub>) (type B), (3) mono-phase liquid (type C), and (4) mono-phase vapor (type D). By the reason of size (moderately between 10 and 30 μm) and position in host mineral, microthermometric analyses generally, have been measured only on primary inclusions of type A and B. The first ice temperature of melting (Te) in type A, often occurs around -24.5° to -19.5° C, corresponding to stable eutectic melting in the NaCl-MgCl<sub>2</sub>-CaCl<sub>2</sub>-H<sub>2</sub>O system. Salinities determined by last ice temperature of melting (Tm) were 3.5 to 15 weight percent NaCl equivalent for inclusions trapped in whole quartz samples. The average of homogenization temperature (Th) values change between 300° and 345°C and Tm measurements range from -11.3° to -3.5°C. The obtained homogenization temperatures for primary types of fluid inclusions may indicate episodes of hydrothermal activities in mesothermal systems for Fe deposits in this region. Type B inclusions, characterized by much more gas bubble within an aqueous liquid are commonly found in all selected samples. Carbonic liquid is seen as a visible immiscible phase within H<sub>2</sub>O liquid. In this type, liquid-CO<sub>2</sub> homogenizes to vapor in the temperature ranging 396° to 410°C. A general increase in Th values is observed for type B inclusions in comparison to type A. The values of Tm in type B inclusions fall within a narrow range from -54.9 to -55.4°C. The fluids consist of mixtures of H<sub>2</sub>O and CO<sub>2</sub>, the most common fluids released during metamorphic reactions [9]. The source of the fluids (magmatic or metamorphic origin) could not be unequivocally determined from the available data; nevertheless, the distribution of fluid inclusions in (Th)-salinity diagram [10], with lines of constant fluid density imply that cooling and increasing of pH, effervescence and fluid mixing, may played an important role in the formation of the Qatruyeh iron occurrences (Fig. 6).

### 4. Conclusion

Based on ore mineral and alteration assemblages, the mineralization and hydrothermal alteration have been divided into two stages: (I) layered magnetite ore stage with sodic- calcic alteration, and (II) hematite ore stage with propylitic-sericitic alteration. Stage I involves the formation of the layered magnetite ores, replacement textures and the formation of titanite+amphibole+siderite+paragonite±tourmaline±quartz assemblages at high temperature hydrothermal activity. Stage II associated with hematite ores and brecciated textures are shown by low temperature oxidizing-hydrothermal fluids and epidote+chlorite+sericite assemblage in shallow levels due to cooling and fluid mixing at this stage. Trace elements contents of the metamorphosed carbonate host rocks shows that HFSEs and HREEs were immobile, whereas LILEs were depleted during the alterations. Fluid inclusion data suggest that low to moderate saline fluids (5 to 15 wt. % NaCl equiv.) were possibly responsible for the development of low-grade magnetite ores. The fluid temperatures are determined between 180 and 435 °C. Increase in pH due to effervescence, fluid mixing and cooling can be effective mechanisms of precipitation of low grade magnetite ores from chloride-bearing hydrothermal fluids.

### 5. References

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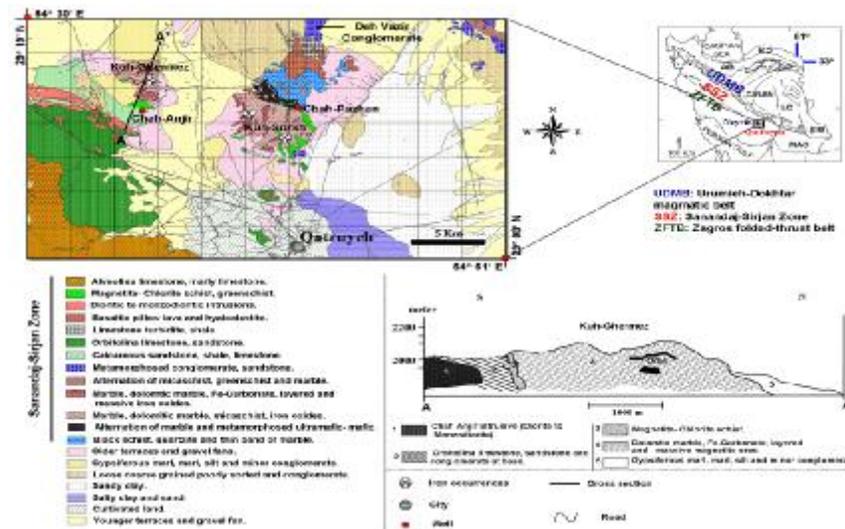


Fig. 1. Schematic geological map of Qatryeh area and tectonic scheme of Iran and interpretative cross section A-A' from South to North.

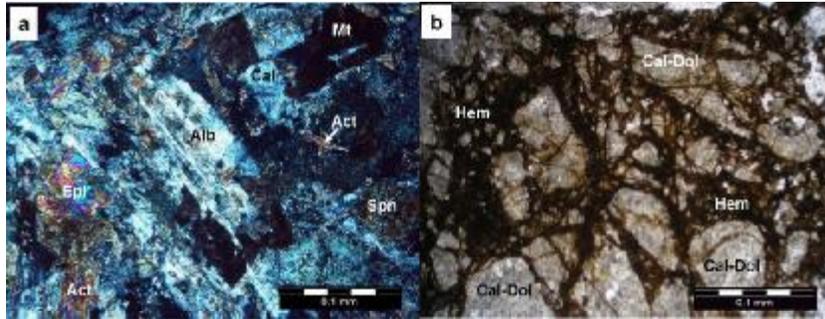


Fig. 2. (a) Mineral assemblages of Na-Ca metasomatism in plutonic rocks. Albite (Alb)+ titanite (Spn)+ epidote(Epi)+ actinolite(Act)+ calcite(Cal)+ magnetite(Mt) (XPL). (b) A host-breccia (cataclastic texture), crashed calcite with hematite(Hem) matrix (PPL).

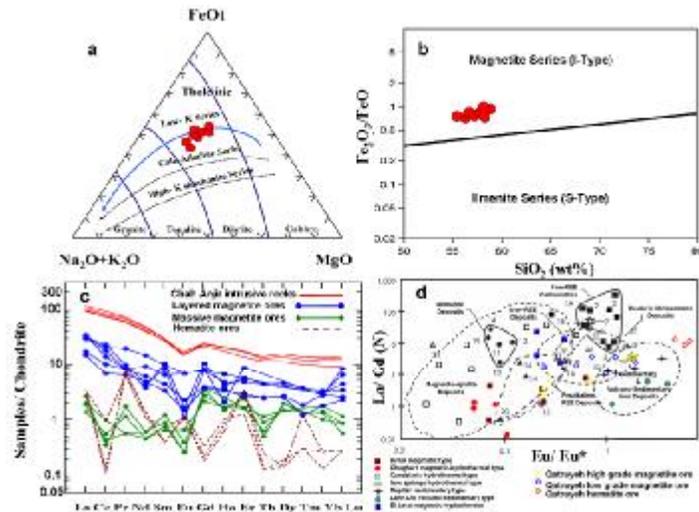


Fig. 3. (a) AFM diagram for determining sub-magma type (calc-alkaline to tholeiitic series), (b)  $SiO_2-Fe_2O_3/FeO$  variation diagram showing fields for magnetite series and ilmenite series granites and intrusive rocks associated with hydrothermal iron deposits, (c) Chondrite-normalized REE distribution pattern of Qatruyeh samples (Chah Anjir intrusive, layered magnetite ores, massive magnetite ores and hematite ores) (d) Plot of La/Gd against  $Eu/Eu^*$  for determination of different type of Qatruyeh iron ores [8].

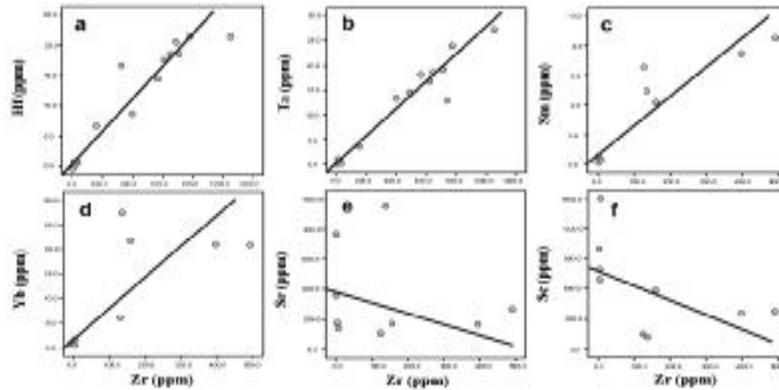


Fig. 13. Binary trace element plots for dolomitic-marble samples of Qatruyeh area. (a) and (b). High field strength elements (Ta and Hf), (c) and (d). Rare earth elements (Yb and Sm) and (e) and (f). Large ion lithophile elements (Sr and Sc).

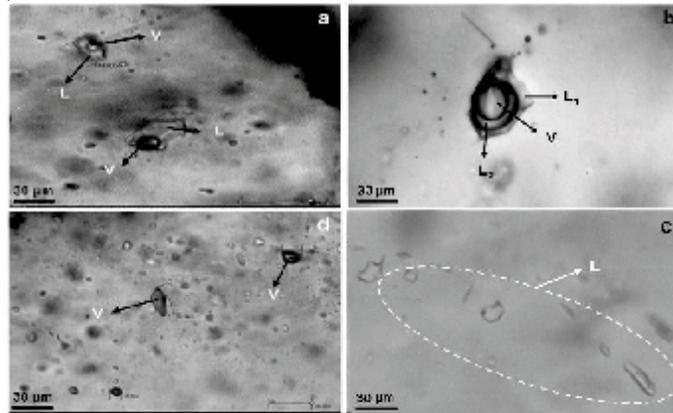


Fig. 5. Photomicrographs of different fluid inclusions in quartz from layered magnetite at Qatruyeh (crossed nicols): (a) fluid inclusions with two phase liquid+vapor (type A); (b) fluid inclusions with three-phase vapor+ liquid (L<sub>1</sub>)+CO<sub>2</sub> liquid (L<sub>2</sub>) (type B); (c) fluid inclusions with mono-phase liquid (type C); (d) fluid inclusions with mono-phase vapor (type D).

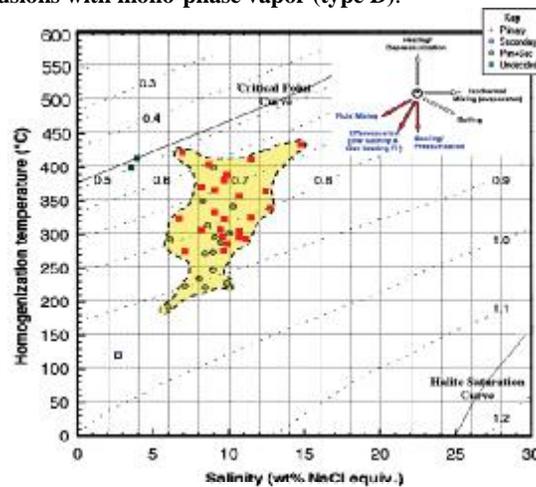


Fig. 6. The most important factors for iron precipitation at Qatruyeh area in homogenization temperature (Th)-salinity diagram [10].