

Ferricretes of the Early Tertiary Dammam Formation in the Dukhan Area, Western Qatar: mineralogy, geochemistry and environment of deposition

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عناقيد الحديد في تكوين الدمام من العصر الثلاثي السفلي في منطقة دخان: معادن، جيوكيمياء وظروف ترسيبها

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هارالد ديل - الهيئة الجيولوجية الألمانية - هانوفر - ألمانيا

تم دراسة عناقيد الحديد المتواجدة ضمن تكوين الدمام من العصر الايوسيني الأوسط بواسطة المجهر المستقطب والعاكس، الاشعة تحت الحمراء، التفاضل الحراري والتحليل الكيميائي. تتكون العناقيد بشكل رئيسي من الجوثيت الذي يوجد على هيئات متعددة وبنيات مختلفة. تدل التحاليل الجيوكيميائية على احتواء العاقيد على رسوبيات كيميائية، هيدروكسيدات الحديد وكميات مختلفة من الكربونات والمواد السليكاتية. تتشابه العناقيد من الناحية المعدنية والنسيجية والكيميائية مع الرسوبيات الحديدية كما وصفت تحت اسم سحنة الفردين. تدل العناقيد الموجودة في طين المدرا على بيئة ترسيب مختزلة خلال العصر الثلاثي في منطقة دخان. كما تدل هذه العناقيد على الظروف المناخية حيث أن الصخور الكلسية الحاوية عليها قد صعدت للأعلى بانتظام خلال العصر الثلاثي العلوي والعصر الرباعي.

Key Words: *Dukhan, Qatar, Dammam, Ferricrete, Mineralogy, Geochemistry*

ABSTRACT

Ferricretes of the Middle Eocene Dammam Formation, Western Qatar, were investigated using petrographic and ore microscopy, IR TGA, XRD, and geochemical analyses. The ferricretes mainly consist of goethite, which is very variegated in habit and texture. Geochemical analyses show that the ferricretes consist of impure chemical sediments, iron hydroxides plus variable amounts of carbonate and siliciclastic materials. The ferricretes resemble with respect to texture, mineralogy and chemistry modern ferrous sediments described as verdine facies. The ferricretes found within the Midra Shale are indicative of a reducing environment of deposition to have occurred during the early Tertiary in the Dukhan Area. These duricrusts may also be used to put some constraints on the climatic conditions as these marine calcareous host rocks gradually emerged during the Late Tertiary and Quaternary.

Introduction

Sedimentpetrographers have paid much attention to encrustations such as calcretes, apicretes or ferricretes in the various continental terrigenous depositional systems and different (paleo) climatic conditions [1-10]. Modern occurrences of goethite-rich sediments are known on the Mahakam delta [11-12], near Margarita Island [13] and the Lake Chad [14]. Odin [12] proposed the term verdine facies to describe these modern goethite-rich sedimentation. Odin and Gupta [15] estimated an ambient sea-water temperature of 20-25°C and a depth range of 0-20 m.

Tertiary sediments are largely exposed across the western part of Qatar, especially at Dukhan area. During the early Tertiary, sedimentation took place in a shallow marine environment. Several transgressive and regressive stages may be recognized in the sedimentary record [16]. The Middle Eocene Dammam Formation of the Dukhan area, Western Qatar (Fig. 1), include scattered outcrops of ironstone nodules.

The purpose of this paper is to investigate these iron nodules through mineralogical and geochemical methods and to determine their environment of formation.

Geological Setting

Qatar forms an exposed part of the Arabian shelf between the Arabian shield and the mobile belt of Iran. It is centered at about 25° N, 51° E. Topographically, Qatar has a low relief landscape with a maximum elevation of about 103 meters above sea level. Structurally, Qatar appears as an elliptical anticlinal arch with a N-S main axis (Fig. 1). The exposed geological succession is made up of Tertiary limestones and dolomites with interbedded clays, shale, gypsum and marls, covered in places by a series of Quaternary and recent deposits [17]. Major faulting is not observed in the studied area. The Tertiary sedimentation

started in Qatar with a marine transgression in the Paleocene. Shallow marine to sabkha conditions prevailed until the end of the Eocene; a carbonate-evaporite sequence (Rus and Dammam Formation) was deposited during this period. The sea regressed at the end of Eocene. A widespread unconformity, causing the absence of Oligocene deposits over most of the area, marked the event. In Qatar, the early Middle Eocene outcrops are represented by the Rus and Dammam formations [17-18]. The Dammam Formation is part of the Hasa Group which consists of the Umm Er Radhuma, Rus and Dammam Formations [18]. Vertically upward in the stratigraphic sequence, the Middle Eocene Dammam Formation is succeeded by the Miocene Dam Formation [16,19]. For the Oligocene, a hiatus in the sedimentary record has been claimed [19]. Cavalier [17], introduced the first stratigraphic attempt and subdivided the Dammam Formation into two informal subformations: the lower Dammam subformation and the upper Dammam subformation. Abu-Zeid and Boukhary [18], renamed the Dammam Formation and subdivided it into four formal members: the Midra Shale, the Dukhan, the Umm Bab and the Abaruq members. The Dammam Formation consists at the base of compact claystone (Midra Shale Member) followed by hard limestone (Dukhan Member) changing to dolomitic limestone (Umm Bab Member) and ended with marly dolomitic limestone (Abaruq Member; Fig. 2). The Midra Shale member is exposed only in southwest and central Qatar. The thickness of this unit ranges between 2 to about 6 m. It is composed of soft, gray, light green, fossiliferous, calcareous, and gypsiferous shale and claystone. Few thin horizons of marls and argillaceous limestones are recorded at the base of the member. The ferricretes crop out as a continuous thin layer of 10-30 cm thick within the upper part of the Midra shale (Fig. 2).

Methodology

The specimens were sampled from the Midra Shale of Dammam Formation in the Dukhan area of western Qatar. About 100 nodules were selected in the field. The samples were studied by X-ray powder diffraction, Infra-red spectroscopy (IR), thermal gravimetric analyses (TGA) and optical microscopy. Infra-red spectrometry measurements were performed using a Perkin Elmer spectrometer. The spectra were recorded at room temperature. Thermal gravimetric analyses were carried out in the range between 30 and 700°C at 10°C/min. Major and trace elements were determined by XRF analyses using a Philips PW-1400 spectrometer. FeO content was determined by dissolving rock powder in a platinum crucible with sulfuric and hydrofluoric acid and titrating the resulting solution with potassium permanganate. Loss on ignition (LOI) was determined after heating at 900°C.

Results

The ferricretes occur as rounded nodules which range in size between 1 and 4 cm (Fig. 3). Microscopic studies revealed that the nodular encrustations from the Midra Shale, Dukhan area mainly consist of aggregates of iron-oxide hydrates different in size and composition. The major iron mineral in the concretions is goethite (α FeOOH) which occurs in subhedral and euhedral grains of as much as 3 mm. In some places, lepidocrocite (γ FeOOH) may be discovered. This modification may be distinguished from goethite by its ruby red internal reflections. In comparison, goethite has yellow brown to reddish brown internal reflections.

Based on their textures, three principal types of iron-oxide hydrates may be identified in the encrustations under study. Collomorphous and boxwork textures are the most common textural types (type I) (Fig. 4). Locally a vague wavy to flakey lamination may be recognized under the microscope (Fig. 4).

Second most in abundance are cubes made up of iron-oxide hydrates. Type IIa occurs in densely packed isometric crystal aggregates. The maximum crystal size in these aggregates is approx. 500 μ m (Fig. 5). The cubic crystals display zones of different shades of

bright and dark brown. Type IIb is similar to type IIa with respect to the crystal size and habit but different with respect to its internal texture. Cubic crystals of type IIb are lining vugs and cracks in the ferricretes. In contrast to type IIa, type IIb aggregates are homogeneous and do not disclose any internal texture. The investigated nodules are oo'id free similar to the modern ironstones described by Odin [12].

Non-ferrous minerals are scarce in the mineral association of the ferricretes. Some illite flakes disseminated in type I iron-oxide hydrate were preserved from limonitization. The majority of phyllosilicates is concentrated in vugs as open space filling. It is kaolinite and some mica, which were spotted under the petrographic microscope. This group of sheet silicates is younger than the process of limonitization.

Figure 6 shows the XRD pattern of the sample which was studied in the range $5-80^\circ 2\theta$, where the most intense reflections of ferric iron oxide and hydroxide phases appear. The data support the mineralogical observations that the nodules are composed mainly of goethite.

Figure 7 portrays the IR-spectra of some ferricretes representative of these Fe-bearing nodules. The most intense peaks of iron oxides and iron hydroxides appear in the spectral range 450-4000 cm^{-1} [20]. Based on IR scattering goethite can be distinguished through the position of the peaks near 450, 600, 794, 888, 1627 and 3422 cm^{-1} , whereas hematite has its most diagnostic peaks at 500, 612 and 1100 cm^{-1} . The IR spectrum of goethite resembles the already published spectroscopic data on this minerals [21, 22]

The thermal and thermogravimetric characteristics of a representative sample is given in Fig. 8. Temperatures of endothermic and exothermic reactions are characterized by the temperature at the crest of

their peaks. In the ferricrete sample, four endothermic peaks are found; three small peaks occur at 70.7 ° C, 123.4 ° C and 203.6 ° C, and the fourth is large and occurs at 299.4 ° C. The first three peaks are accompanied by a slight loss in weight (0.06-0.8 %), whilst the fourth major peak is accompanied by a larger loss in weight (5.55 %). The first three peaks are mostly due to the loss of hygroscopic water. The fourth peak is mainly due to the loss of water of crystallization.

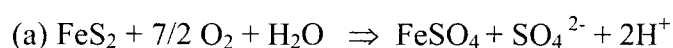
Geochemical analyses (Table 1) indicates that the nodules are variable mixture of a Fe-rich chemical component and an Al-Si-Ca rich detrital component. SiO₂ ranges between 4 to 11 wt. %, Al₂O₃ varies between 3.5 and 6.5 wt. %, MgO ranges between 0.8 to 1.8 wt. %, CaO between 2.6 and 4.5 wt. % and P₂O₅ between 0.15 and 0.25 wt. %. Na₂O and K₂O are very low. The contents of the trace elements Ba, Co, Ni, Cu, Nb, Sr, Y, Zr are below 100 ppm. Goethite is the prevailing mineral of control on the chemical composition. All analyses show a ratio of Fe₂O₃/FeO greater than 1 and very high content of both Fe₂O₃ and LOI.

Discussion

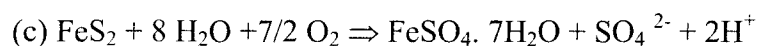
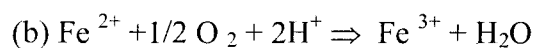
Hematite is mainly formed from the poorly crystallized ferric iron hydroxide ferrihydrite 5Fe₂O₃.9H₂O [23], by topochemical reactions, whereas goethite is formed directly from solution or from ferrihydrite or other iron oxides via a dissolution-precipitation mechanism [24-27].

Type-IIa goethite is pseudomorphosing pyrite cubes. Deposition of the early Tertiary host sediments took place under dysoxic or slightly reducing conditions. Oxidation of Fe disulfide in supergene environments was described mostly in a two-step reaction beginning with the oxidation of sulfur and followed by the oxidation of ferrous iron [28].

Oxidation of sulfur:



Oxidation of ferrous iron:



Lepidocrocite substitutes for goethite when the sulfate concentration is maintained at a very high level during alteration of primary disulfides. One can assume, that the resultant sulfate was quickly removed from the site of alteration so that only in few places lepidocrocite could form or be preserved. Another evidence for this rapid release of sulfate is the lack of Fe sulfate minerals. The first step of oxidation, the conversion of S⁻ in pyrite into S⁶⁺ caused melanterite formation, a hydrated Fe sulfate (FeSO₄.7H₂O). This chemical compound may be found under arid climatic conditions or strong evapotranspiration [16, 29]. Even under the extremely arid conditions during the Late Tertiary and Quaternary in the Region of the Arabian Gulf sulfate were not able to survive for reasons of sulfate-limitation in the supergene system.

Co and Ni are known to be the most common elements that may substitute for Fe in the pyrite lattice. If substitution is taken to completeness it may give rise to minerals such as catterite (CoS_2) or vaesite (NiS_2), respectively. In nature, however, prevalently bravoite with marked growth zones indicating a solid solution of catterite, vaesite and pyrite occurs [30]. Bravoite is frequently observed in sedimentary rocks and in the upper parts of ore shoots containing sulfide. This Ni-Co-Fe solid solution precipitates at the boundary between the zone of cementation and oxidation in gossans above primary sulfide mineralization or near the ground water level in sulfide-bearing sediments. Bravoite was the parent material for type IIa limonite and is assumed to have formed under the influence of a fluctuating ground water table. Kaolinite which is younger than both of these pseudomorphoses developed from acidic meteoric fluids.

Type-I limonite derived from neomorphism of type IIa and IIb limonite. Solution cavities point to strong leaching of the ferricretes during the waning stages of alteration of the original disulfide.

Iron oxides pseudomorphosing pyrite cubes in the Midra Shale are clear evidence that reducing conditions existed in the basin. Decomposition of Fe-bearing clay minerals in the Midra Shales has resulted in the build-up of ferrous concretions and provoked a red and brown staining of sedimentary rocks. As the quantity of ferrous concretions diminishes the red and brown color turns into grey and white whereas the content of carbonate increases towards the top of the Midra Shale. The presence of trivalent iron in the various minerals is not controlled by one unique unconformity but closely reflects the distribution of argillaceous layers, cycles of inferior order ("parasequences") in the Midra Shale and their bounding surfaces. Ferricretes are common on unconformities and frequently encountered in coastal areas where hydrological and pedogenic processes may both have contributed to the precipitation of such encrustations [8, 31].

Ferricretes have been derived from Fe-bearing phyllosilicates and Fe disulfides. Iron-oxide (hydrates) containing Fe (III) are brought about by oxidizing conditions, their parent material, however, furnish evidence of less oxygenated conditions and a rising sea level during the Lutetian transgressive system tract.

Conclusion

Goethite type IIb suggest that the host rocks formed under moderately reducing conditions in a marine environment of deposition. Alteration of pyrite was certainly not a monophasic process which immediately led to the ferrous encrustations scattered all across the present-day surface. Primary pyrite was brought into the reaches of a fluctuating ground water level and transformed into bravoite under climatic conditions which obviously were more humid than the present-day climate. This process is supposed to have taken place very fast. Otherwise these growth zones in goethite IIa would not have been preserved in such a perfect way and completely been converted into a massive or boxwork goethite (type II).

Table 1: Chemical analyses of representative ferricretes from Dukhan area

Sample	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9	H-10
Wt. %										
SiO ₂	4.02	5.65	6.76	7.64	5.62	5.37	9.1	8.81	11.3	9.2
TiO ₂	0.15	0.1	0.12	0.1	0.14	0.16	0.1	0.15	0.08	0.1
Al ₂ O ₃	4.1	3.5	5.15	3.9	3.8	5.15	4.72	4.3	5.3	6.5
Fe ₂ O ₃	37.2	33.3	29.94	29.7	29.8	33.7	32.6	33.4	38.5	40.5
FeO	24.9	24.7	22.6	24.8	24.4	21.9	23.3	24.5	18.4	15.6
MnO	0.05	0.04	0.15	0.17	0.15	0.18	0.16	0.1	0.2	0.33
MgO	0.82	1.1	1.15	1.75	1.8	1.4	1.2	1.1	1.6	1.4
CaO	4.5	3.7	4.15	2.97	2.6	3.8	3.5	2.8	1.33	5.1
Na ₂ O	0.11	0.11	0.15	0.2	0.15	0.18	0.1	0.17	0.08	0.11
K ₂ O	0.01	0.01	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.01
P ₂ O ₅	0.24	0.16	0.22	0.25	0.18	0.14	0.18	0.2	0.15	0.15
LOI	23.1	27.2	28.7	27.6	30.6	27.5	24.23	23.8	22.5	20.6
Total	99.2	99.46	99.1	99.1	99.25	99.5	99.2	99.35	99.45	99.6
ppm										
Ba	21	45	18	20	50	15	60	10	36	42
Co	29	50	30	23	24	20	26	60	27	24
Ni	35	58	45	30	32	35	32	75	34	30
Cu	15	34	16	18	11	7	13	8	8	11
Nb	6	6	8	9	7	5	4	6	5	8
Sr	90	93	97	85	80	37	85	59	33	24
Y	38	28	22	13	25	20	30	25	23	24
Zr	42	40	49	31	55	41	35	32	90	43

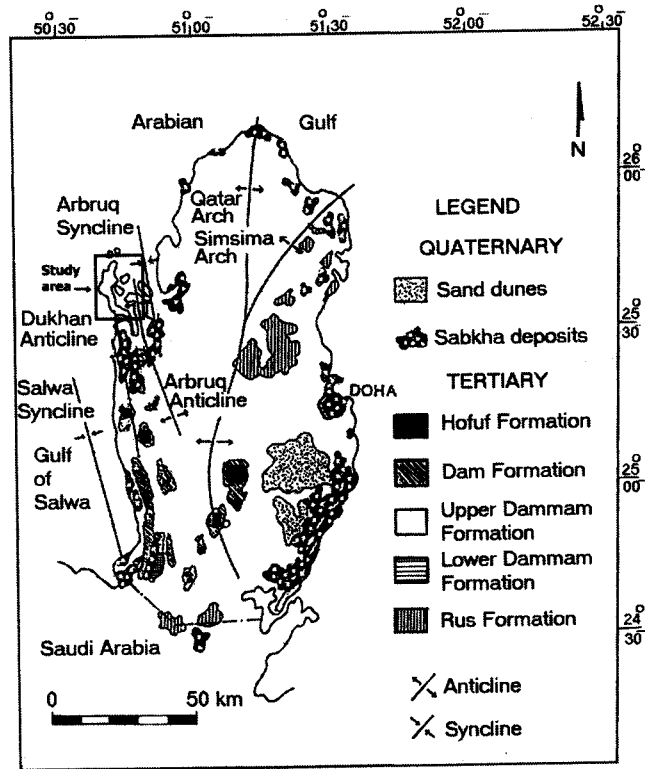


Fig. 1. Geological map of Qatar showing location of the study area.

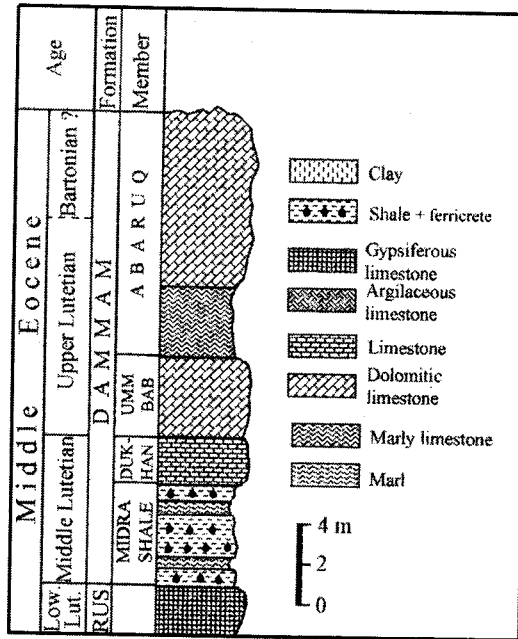


Fig.2 . Stratigraphic section in Dukhan area

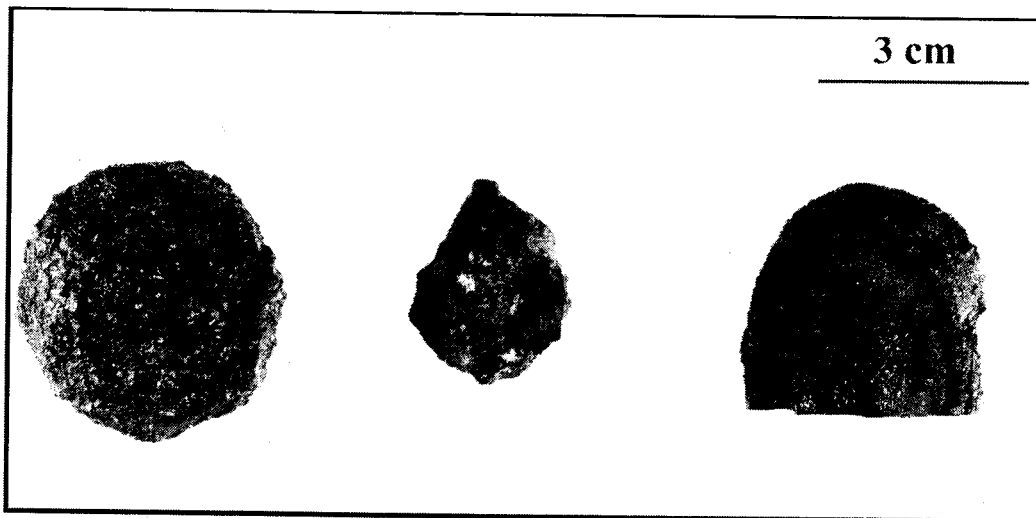


Fig. 3. Representative ferricrets from Dukhan area

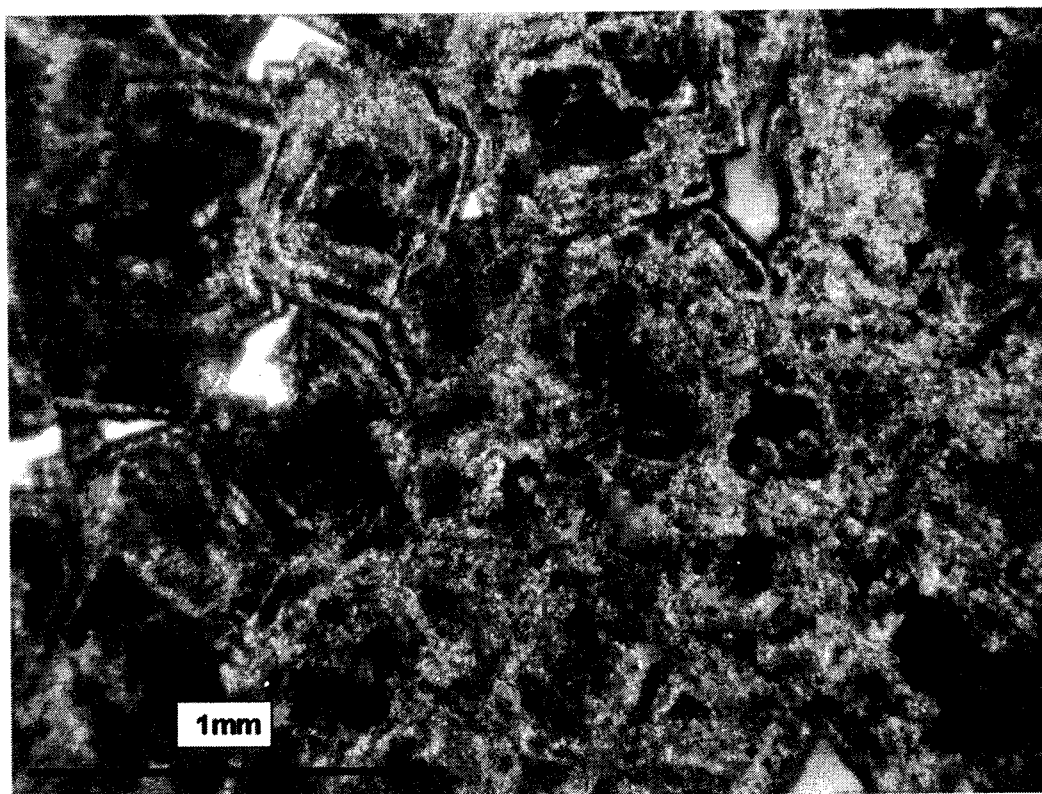


Fig. 4 . Microphotograph showing collomorphic texture of type I ferricretes

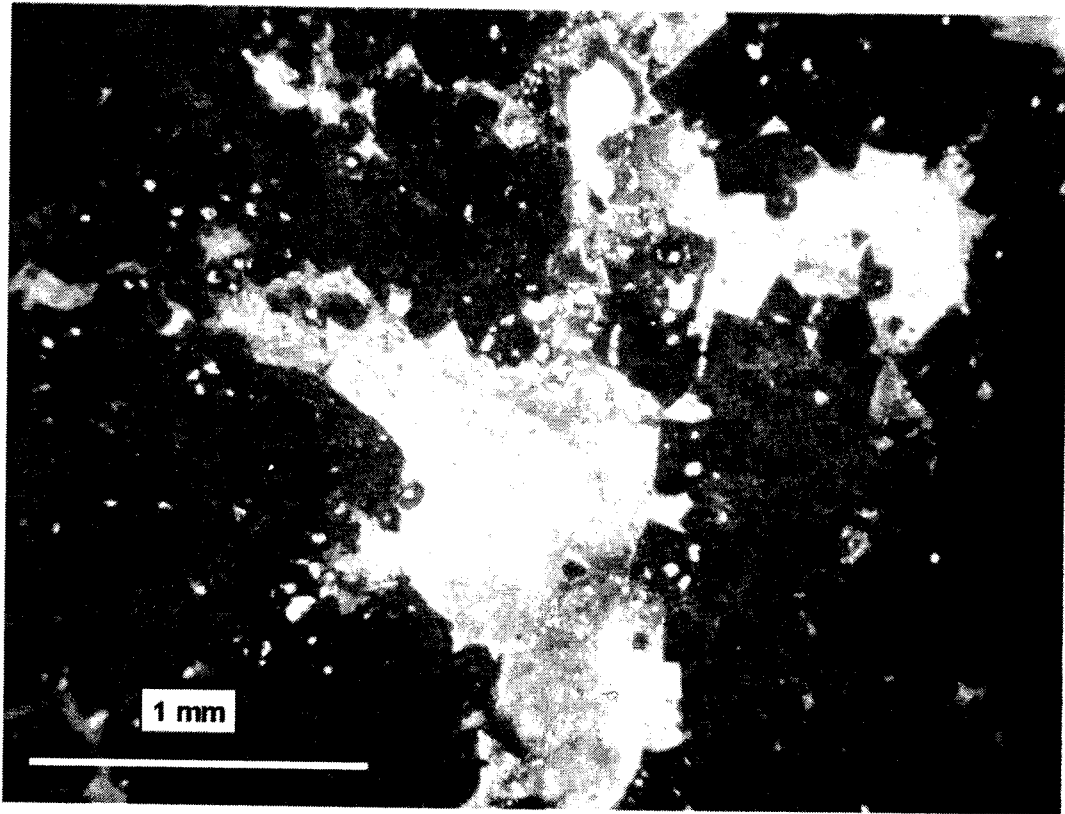


Fig. 5. Microphotograph showing cubic crystal aggregates of type II ferricretes.

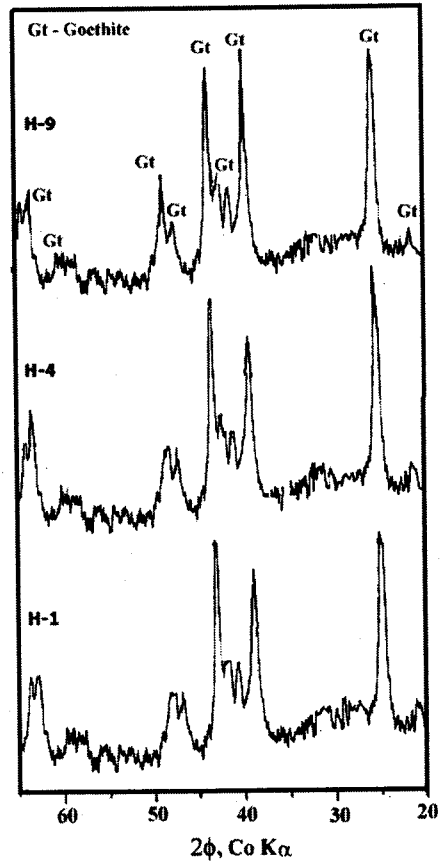


Fig. 6. Representative X-ray diffraction pattern of the ferricretes

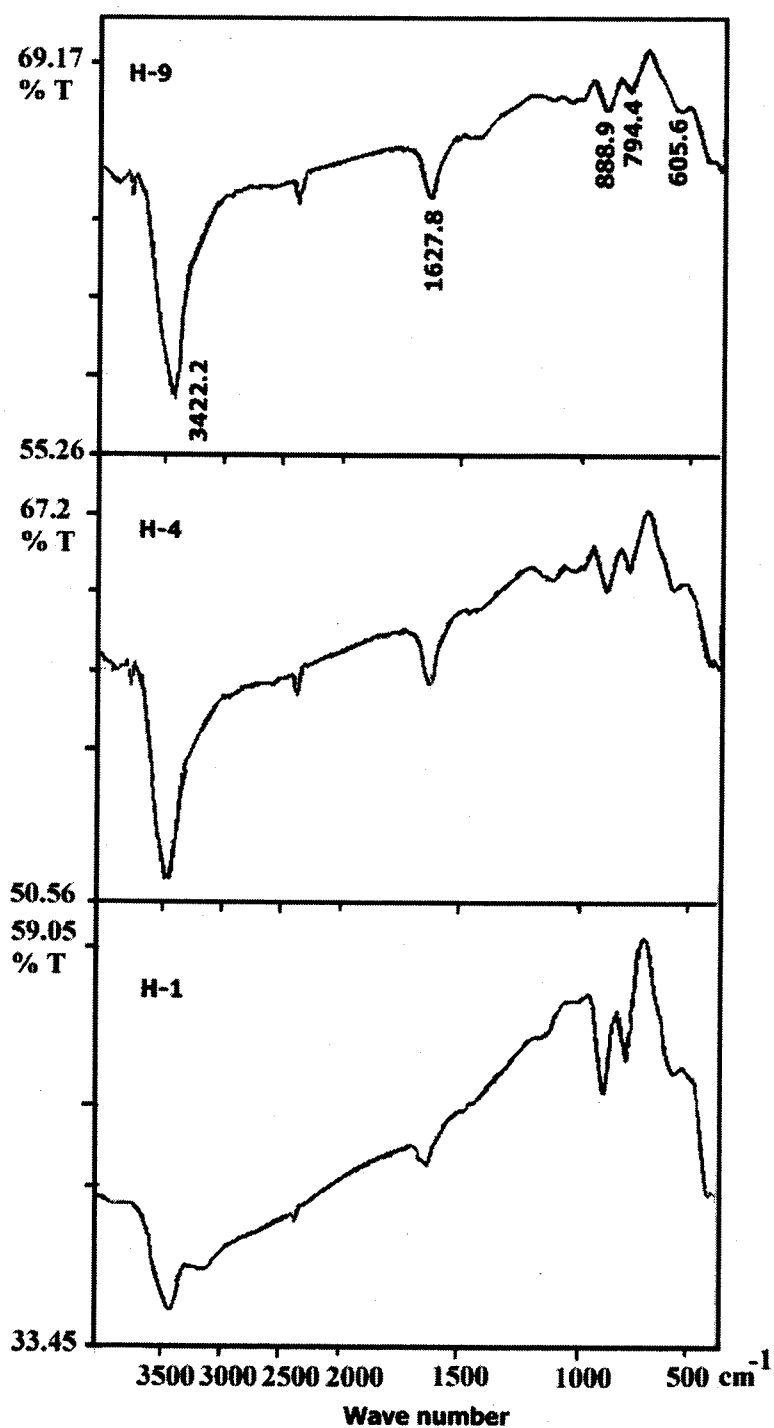


Fig. 7. Representative Infra-Red spectra of the ferricretes. The numbers represent the position of the peaks typical of goethite.

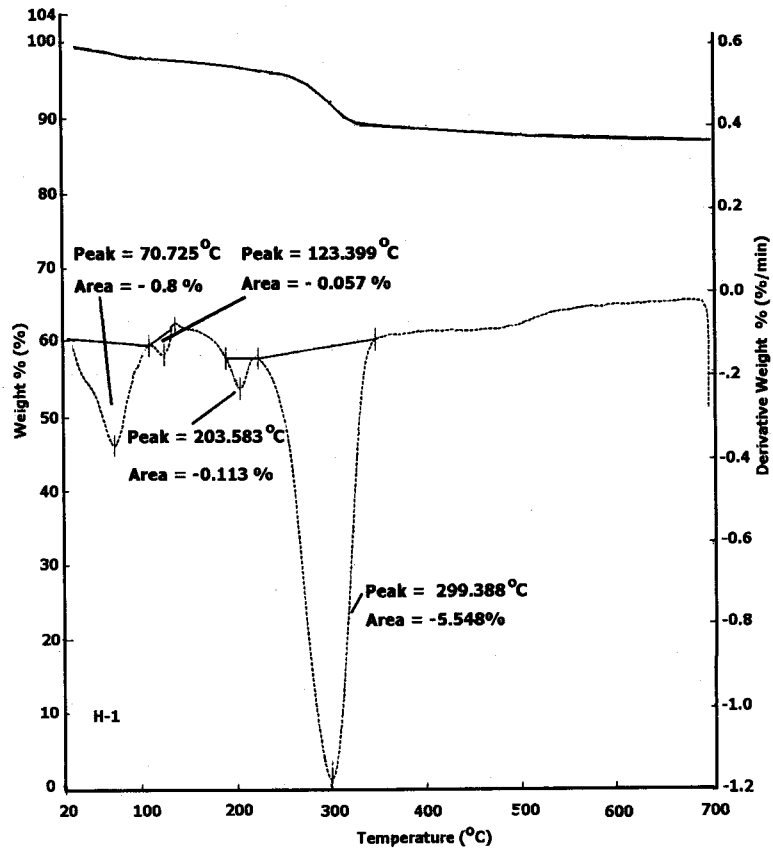


Fig. 8. Representative TGA of the ferricretes.

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