MICROSCOPIC EVIDENCES OF REPLACEMENT OF IRON SULFIDE BY IRON OXIDE IN MACRO FOSSILS: A USEFUL TOOL FOR THE SEARCH OF LIFE IN MARS?. A. Blanco[1*], U. Bolaños-Sánchez[1], L. Lizárraga-Mendiola[2], J. Hernández-Ávila[1], S. Ángeles-Trigueros[1]. S. P. Ambrocio-Cruz[1] M.R. González-Sandoval[3]. [1]Área Académica de Ciencias de la Tierra y Materiales, Universidad Autónoma del Estado de Hidalgo. ([*]blanco.earthsciences@gmail.com). [2]Área Académica de Ingeniería. Universidad Autónoma del Estado de Hidalgo. Mineral de la Reforma, Hidalgo, México. [3] Instituto de Ingeniería. Universidad Nacional Autónoma de Mexico. México, D.F. Mexico

Introduction: The present paper documents the presence of elements such as isolated crystals, framboids and teeth and socket structures in samples of iron oxides collected from macrofossils from the Upper Cretaceous (Turonian) Eagle Ford Formation, cropping out in the vicinity of Muzquiz county, at Coahuila state, northeastern Mexico. At this area, the inner shelf Boquillas Formation consists of at least 6 m of interbedded brown-yellowish marlstone of about 7-15 cm thick and occasional decimetric (10-25 cm) beds of grey limestone. Marlstone exhibits a parallel millimetric-scale lamination associated to microbial activity, and occasionally shows iron oxide minerals exposed on nodules with a diameter of about 3 cm and millimetric layers arranged parallel to the stratiphication plane resembling the distribution of sedimentary pyrite in dysoxic/anoxic sediments. Fossils of macroorganisms consist mainly of bivalves, ammonites and fish, and they present several degrees of preservation. Ocassionally, fossils are completely replaced by iron oxides.

So far, it is known that the iron oxides exposed in the rock strata of some localities are the result of post-diagenetic oxidation of sedimentary pyrite under different geological processes. However, it has been reported that the oxidation process does not destroy the features formed in the sedimentary pyrite, remaining in the matrix of the new iron oxide minerals [1], [2].

Pyritized fossils are relatively common in the stratigraphic record. In fossilized organic remains, when pyrite is present, it can occur as isolated euhedral crystals, or forming clusters and framboids [3], [4], [5], [6]. Pyrite can also expose some features associated to bacterial activity such as wavy lamination, presence of teeth and socket structures or even remains of microfossils [5], [6]. The main purpose of this work is to provide a general description of the primary structures reported in sedimentary pyrite, but present in iron oxide minerals obtained from fossils of macroorganisms coated by iron oxide minerals. We also provide a short discussion about its possible implication in the prospection of extraterrestrial life, specially in Mars.

Methods: Three samples of iron oxide were obtained from an unidentified ammonite collected from the Boquillas Formation at the study area. Samples were broken-up into fragments of 1cc approximately and washed with HCl solution (10%) for removing remains of the surrounding carbonate rock. The fragments were gold coated for three minutes and observed under a scanning electron microscope (SEM) for searching structures. Dispersive X-ray Spectrometry (EDS) analysis were performed for elemental composition.

Results: Whitin the iron oxide samples some isolated crystals, framboids and teeth and socket structures were observed. Isolated crystals do no exceed the 5μm in size being the euhedral forms the most abundant.

In the samples analyzed, also both entire and fragmented framboids were observed. Framboids are formed by close packed equigranular euhedral microcrystallites. They are sub-spheroidal in outline and expose straight edges and flat faces. Their diameter ranges from 5μm to 14μm. On the other hand, fragmented framboids exhibit close packed euhedral crystallites forming a regular honeycomb-like pattern of polygons (Figure 1).

Some parts of the analyzed samples expose smooth surfaces interrupted by several rows of pits. Similar structures are known as "teeth and socket" [5]. The smooth surfaces have been interpreted as the consequence of the replacement of bacterial fluids by minerals [5], such as iron sulfides, whereas the pits represent the spaces in which ehuedral crystals of different sizes (generally of about 1μm) were situated.

EDS analysis revealed the presence of oxygen (O) and iron (Fe), indicating that the structures here described are formed by iron oxides. Beside, the total absence of sulfur (S), in the samples also indicates that no autigenic sedimentary pyrite remained in the fossils.

Discussion: The structures here described consist of isolated euhedral crystals, framboids and teeth and sockets-like elements. So far, it is known that in sedimentary settings all these elements are associated with the formation of pyrite within the sediment [3], or they are formed in the water column, when dysoxic/anoxic conditions are predominant. However, these elements are not associated to iron oxide minerals as a primarily-formed constituents. According to this, the presence of these elements in the fossils from Muzquiz suggests the following: 1) Macro fossils from the vicinity of Muzquiz, northeastern Mexico were originaly preserved under dysoxic/anoxic conditions and replaced by iron sulfides (e.g. sedimentary pyrite) formed during the accumulation of the Eagle Ford Fm. during the Turonian (Late Cretaceous). Later, the iron sulfide was completely replaced by iron oxide minerals as a consequence of posterior geological processes, such as hydrothermal events occurred during the Late Cretaceous. However, some authors have suggested that the oxidation of iron sulfides occur during the later diagenesis. At this stage, the reducing conditions resulting as a consequence of the decomposition of organic matter (OM) are no longer dominant, being the influence of oxidation of host rocks the new predominant conditions [2]. However, most detailed geochemical studies must be carried out in the sediments of the Eagle Ford Formation to confirm either of both hypothesis.

Currently, it is well known that several authors have suggested the presence of pyrite in siliciclastic sediments of ancient Mars. It is considered that the presence of iron oxides (e.g, hematite) in Martian sediments could result from the fotooxidation of iron sulfides under aqueous conditions [7]. In Mars, at Meridiani Planum, for instance, the discovery of jarosite-bearing deposits at the landing site of the Opportunity rover could imply that they were formed as a consequence of the aqueous oxidation of pyrite [8]. In addition, the presence of sulfates in Mars has also been explained as as the possible result of radiolytic oxidation of pyrite [9]. Therefore, it seems that several evidences of the presence of pyrite in Mars exist, however, Did the pyrite from this planet have a sedimentary origin? So far, this question remains unanswered and further geochemical and geological studies must be carried out to determine whether sedimentary pyrite had a chance to be formed and where. But if it did, then the search of microscopic remains in iron oxides that replaced iron sulfides becomes really crucial for detection of ancient life in Mars. Since fossilized microorganisms and other structures formed in pyrite can survive to the oxidation, it is vital to return rock samples with iron oxides from Mars to the Earth. Specially from places in which iron oxides are in sediments interpreted as lacustrine or even marine, to try to identify in such samples some biotic elements commonly present in the sedimentary pyrite. This could provide to the astrobiologists a new insight in the search for life in the Red Planet.

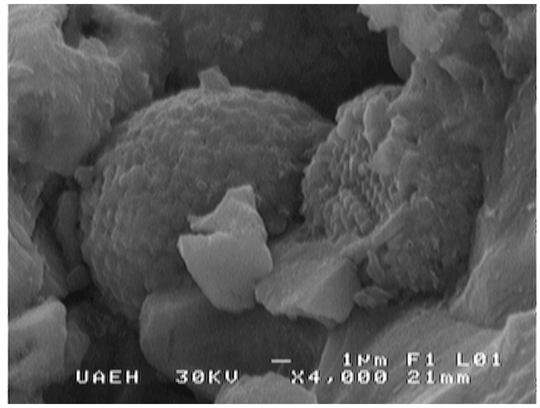

Figure 1. SEM Image of framboids and regular honeycomb pattern of polygons present in the iron oxides from the Eagle Ford Formation.

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