Geochemistry and Mineralogy of Jurassic Manganese Crust from Jbel Moussa Group (Rifian Domain, Morocco): Hydrothermal Origin

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INTRODUCTION.

Hydrothermal manganese deposits not directly associated to oceanic crust settings, are also known as linked with fault zones. The stratigraphic record of the Middle and Upper Jurassic in the western Tethys is characterized by common eustatic and tectonic events recorded as stratigraphic unconformities, represented by hardgrounds, palaeokarsts, palaeosoils and the deposition of Fe-Mn and/or phosphatic crusts. The present paper is focused in the mineralogical and geochemical characterization of a manganese crust of the Jbel Moussa Group (Rifian Domain, Northern Morocco). The characterization of the crust from mineralogy, geochemistry and microstructures including microbial fabrics, allows determining the genetic type (hydrothermal, hydrogenetic or diagenetic).

GEOLOGICAL SETTING.

The Jurassic manganese crust studied crops out in the northernmost end of the Rifian Calcareous Chain (Rifian Dorsale Calcaire), an area belonging to the so-called Jbel Moussa Group. Precisely, the studied manganese crust occurs in the western part of the Ras Leona High, close to an old mining site located 1.5 km west of Beliounis village. The manganese crust lies between Lower Jurassic massive limestones and the overlying Upper Jurassic radiolarites, which are separated by palaeokarstic surface with neptunian dykes. The studied discontinuity surface corresponds to Upper Bajocian (El Kadiri, 2002).

During the Jurassic, the Alboran Margin was submitted to extension with individualization of blocks. The maximum differentiation of blocks into different palaeogeographic domains represented by the Rif occurred during the Middle and Late Jurassic, resulting in rotational tilting of the blocks.

METHODS.

Petrographic microscopy was used to determine the textures of the manganese crust. The mineral composition of the crust was determined by X-ray diffractometry (XRD) in the Universidad de Jaén. Carbon-coated and gold-coated polished thin-sections were examined under scanning electron microscopy (SEM) using back-scattered electron (BSE) imaging and energy-dispersive X-ray (EDX) analysis in order to obtain textural and chemical data, at the Universidad de Granada.

Mn crusts were split and the broken pieces from the inner surfaces of the crust were mounted, coated with carbon or gold, and examined directly under the SEM using secondary electrons to study their internal structure and crystal morphology at the Centro Andaluz de Medio Ambiente.

Whole-rock analyses of major elements of the crust were carried out using X-ray fluorescence (XRF). Trace elements were analysed using an inductively coupled plasma-mass spectrometer (ICP-MS) at the Universidad de Granada.

MANGANESE CRUSTS.

The discontinuity surface is characterised by the record of 1–10 cm thick black crust with metallic shine. To our knowledge, this is the thickest crust discovered in the Betic-Rifian Cordillera until now. Under the microscope, the crust has a poorly developed laminated structure. Below the thick manganese crust the manganese minerals progress downward in the limestones, from the discontinuity surface favoured by microfissures. Under SEM analysis, the irregular lamination ranges between 3–20 μm thick per laminae. Two types of planar laminae can be differentiated:

- Crystalline planar laminae: 10–20 μm thick and made of both small acicular and sheet crystals.

- Microbial planar laminae: 3–8 μm thick and constituted by a dense web of filaments.

GEOCHEMICAL AND MINERALOGICAL COMPOSITION.

The most abundant component is MnO (72.0% by weight). Other main components are SiO_2 (2.3%), CaO (1.7%), K_2O (1.1%), MgO (1.1%), Fe_2O_3 (0.8), and Al_2O_3 (0.8%). The crust presents an evident enrichment in Sr, Ba, Co, Ni, and Cu as compared to the bulk composition of the upper continental crust (Post-Archean Australian Shales PAAS, of Taylor & McLennan, 1985). The PAAS-normalized patterns show a negative Ce anomaly and a positive Eu anomaly. The manganese crust is basically composed by Ca-birnessite, cryptomelane, and coronadite.

MICROBIOTA.

The SEM analyses of the microbial planar laminae of the Mn crusts allowed us to characterize three types of microbial structures made up by Mn mineral: a) Filaments with dense dichotomous branching ranging between 2.2–4.2 μm in diameter and more than 60 μm in length, locally with trichomal arrangement; b) simple filaments <1.8 mm in diameter and larger than 60 μm; and c) coccoid-shaped forms with a size of 1.7–3.0 μm. Some samples are composed exclusively by filamentous microbial meshworks.

palabras clave: Discontinuidad, Quimiosíntesis, Microbios, REE. | *key words:* Discontinuity, Chemosynthesis, Microbes, REE.

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DISCUSSION.

The mineralogy and the geochemistry of this Mn crust are congruent with a hydrothermal origin. According to Glasby (2000) the hydrothermal Mn-crusts in the recent oceans are characterized by low contents (in ppm) of Cu (20-1000), Ni (1-1400), Zn (1-1230), Co (6-210), and Pb (0-93). The manganese crust from Ras Leona section presents values included in the hydrothermal range for these elements (in ppm, Cu= 200, Ni= 130, Zn= 95, Co= 86, and Pb= 2).

Mn/Fe ratio exceeds 40, which is typical of hydrothermal manganese crusts (Usui et al., 1997). In the studied example the Mn/Fe ratio is 87. Negative Ce anomaly, positive Eu anomaly and low $\sum$REE are characteristic of hydrothermal manganese crusts (Kuhn et al., 1998). High Eu anomalies in the deposits confirm the leaching of the divalent Eu^{2+} from the host rocks took place at temperatures greater than 250ºC. Enrichment in Low REE relative to High REE is other indicator of hydrothermal origin (Mills & Eldefield, 1995).

The identified minerals (Ca-birnessite, cryptomelane and coronadite) have been interpreted in relation to hydrothermal vents (Lonsdale et al., 1980; Glasby et al., 2005; Canet & Prol-Ledesma, 2007).

In this context, the record of benthic microbial communities is congruent. Modern microbialite mats occur abundantly in the vicinity of submarine hydrothermal vents and cold seeps, which are the source of nutrients for microbes. Microbes that precipitate Mn oxides and iron compounds were described from those environments (Mandernack & Tebo 1993; Ehrlich 1996; Connell et al., 2009; Santelli, 2009; Templeton et al., 2009). We interpret the precipitation of manganese minerals as induced by chemoorganotrophic behaviour of benthic microbial communities, since manganese oxides can form as a result of the direct metabolic activity of microbes (Ehrlich, 1996; Chafetz et al., 1998; Frankel & Bazylinski, 2003). A high microbial activity has been described in hydrothermal vents where microbes enhance the scavenging of Mn and facilitate Mn deposition (Mandernack & Tebo, 1993).

Thin section examination allowed us to interpret episodes of Mn impregnation of the underlying sediment from the crust favoured by fractures and porosity of the limestone. Its related mineralization processes affected only the top of the limestones and advanced downwards through epigenesis, sometimes over 40 cm in depth, probably related to removilization of minerals during the diagenesis.

The palaeogeographic evolution of the Jbel Moussa Group (El Kadiri, 2002) evidences a strong tectonic influence during the Jurassic. This leads us to postulate a local normal fault system of Jurassic age in Rifian Calcareous Chain and concretely in the Jbel Moussa Group, along which the hydrothermal solutions arrived from the underlying continental basement.

CONCLUSIONS.

Manganese crusts from Middle Jurassic-Upper Jurassic discontinuity of the Jbel Moussa Group (Rifian Cordillera) are composed by Ca-birnessite, cryptomelane and coronadite. The ores with Mn grades up to 70 wt% MnO, have a negative Ce anomaly and a positive Eu anomaly.

Microbial structures are densely present in the lamination and they were probably involved in the precipitation of Mn with chemosynthetic behaviour.

Mineralogical and geochemical features, together with the presence of microbial structures suggest that this Mn ore deposits formed as a result of venting hydrothermal fluids, through sinsedimentary faults. Microbes have been registered in relation to recent Mn-rich deposits associated from black smokers to cold seeps, with affinity for extreme ecological conditions.

It seems therefore that the deposition of the Mn crust was controlled dominantly by the activity of a submarine hydrothermal fault-controlled vent, which was the main source of Mn.

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