Hydrothermal and Hydrogenetic Origins of the Middle Jurassic Fe and Mn Crusts from Betic-Rifian Cordillera Based on Geochemical Analyses

/ ISABEL ABAD (*), MATÍAS REOLID

Departamento de Geología, Universidad de Jaén, Campus Las Lagunillas sn. 23071, Jaén (Spain)

INTRODUCTION

The Middle-Upper Jurassic transition within the External Subbetic (Betic Cordillera, Southern Spain) and the Jbel Moussa and Jbel Juimâa groups (Rifian Calcareous Chain, Morocco) is characterized by numerous stratigraphic breaks recorded as palaeoreliefs, omission surfaces, and hardgrounds. The features and number of unconformities vary depending on the domain studied and the tectonic unit. One common characteristic is the presence of microbial Fe-Mn crusts (Reolid, 2011).

This research is focused on the review and comparison of the genetic types (hydrothermal or hydrogenetic) of Fe-Mn crusts from hardground surfaces related to the Middle-Upper Jurassic boundary based on a geochemical study. The data presented are the result of a study of Fe-Mn crusts from 6 outcrops: 1 section from the Central External Subbetic (Cabra), 3 sections from the Eastern External Subbetic (Lúgar 1, Lúgar 2, and Quípar), and 2 sections from the Rifian Calcareous Chain (Ras Leona from Jbel Moussa Group and Onzar from Jbel Juimâa Group). XRD was used for mineral determination, SEM (BSE imaging and EDX) for mineral, chemical, and textural data and XRF/ICP-MS for whole-rock analyses of major and trace elements respectively.

MINERALOGY AND GEOCHEMISTRY

Two main types of crusts can be differentiated: Fe-rich crusts and Mn-rich crusts (Table 1).

Fe-Rich Crusts

The Fe-rich crusts developed on different Middle Jurassic hardgrounds (the Lower-Middle Bathonian HG, the Middle-Upper Bathonian HG, and the Callovian-Oxfordian HG) and also growing in the walls of neptunian dykes and sills related to these surfaces. The crusts are < 5 cm thick and three morphological types of laminated crusts are registered: stromatolites, macro-oncoids, and endostromatolites (submarine cavity and fissure dwelling stromatolites).

The crusts studied in the Central External Subbetic (Córdoba Province) are constituted mainly by goethite and calcite, with a Fe_2O_3 content between 4 and 20 wt.% and < 7 wt.% of MnO (Table 1). The chondrite-normalized REE patterns, using the CI carbonaceous chondrite (McDonough & Sun, 1995), show a clearly positive anomaly of Ce (Ce/Ce*=3.11). The $\sum$REE content (449–2083 ppm) is higher than in the upper continental crust (183 ppm) referred to Post-Archaean Australian Shales (PAAS; Taylor & McLennan, 1985).

The crusts from Eastern External Subbetic (Murcia and Alicante provinces) are made up of goethite, calcite, lithiophorite, and cryptomelane (Jiménez-Millán & Nieto, 2008). The Fe_2O_3 proportion in crust and macro-oncoids is between 9 and 20 wt.%. The MnO content is always < 1.5 wt.% (Table 1). The crusts are enriched in Co, Ni, As, and Sb, while the $\sum$REE content (652–850 ppm) is close to the hydrogenetic recent Fe-Mn crusts (Fleet, 1983). These crusts present a positive anomaly in Ce (Ce/Ce*=7.26).

The crusts from Jbel Juimâa Group (Rifian Calcareous Chain) are composed mainly by goethite and calcite. The Fe_2O_3 proportion is 17.5 wt.%, whereas SiO_2 presents highest values (16.3 wt.%) compared with the other studied outcrops. These crusts also present a positive anomaly in Ce (Ce/Ce*=4.26) with $\sum$REE in the crust (309 ppm) higher than in PAAS.

Mn-Rich Crusts

The Mn-rich crusts are located in Jbel Moussa Group (Rifian Calcareous Chain) represented by poorly laminated black crusts with 1–10 cm thick. Under the petrographic microscope, the crusts have a poorly developed laminated structure. X-ray diffractograms and EDX analyses reveal that they are basically constituted by manganese oxides: Ca-birnessite, cryptomelane and coronadite (Reolid et al., 2011).

The bulk chemical composition of the crusts is characterized by a high content of MnO (72.0 wt.%). Other major components are SiO_2 (2.3%), CaO (1.7%), K_2O (1.1%), and MgO (1.1%). Fe_2O_3 and Al_2O_3 are < 1%. In addition, the crusts present significant

	Cabra	Lúgar 1	Lúgar 2	Quípar	Onzar	Ras Leona
Mineralogy	Gth, Cal	Gth, Cal, Crp, Ltp			Gth, Cal	Brn, Crp, Cor
Fe₂O₃ (wt.%)	4-20	9-20			17.50	< 1
MnO (wt.%)	0.81-6.48	0.05-1.46			0.17	72.0
∑REE (ppm)	449-2083	652-850			309	11
*Ce/Ce**	positive	positive			positive	negative

Table 1. Main mineralogical and geochemical results of the crusts studied. Brn: Birnessite, Cal: Calcite, Cor: Coronadite, Crp: Cryptomelane, Gth: Goethite, Ltp: Lithiophorite.

enrichments in Sr (1140 ppm), Ba (2125 ppm), Co (87 ppm), Ni (131 ppm), and Cu (201 ppm) respect to the bulk composition of the PAAS. The ∑REE (11 ppm) is very low and the light REE are more abundant than heavy REE. The chondrite-normalized REE patterns show two anomalies: one negative in Ce (Ce/Ce*= 0.56) and one positive in Eu (Eu/Eu*= 4.60).

INTERPRETATION

According to mineralogy and mainly geochemistry of the crusts, two different genetic contexts can be differentiated: hydrogenetic and hydrothermal. Hydrogenetic crusts form directly from seawater in an oxidizing environment (Glasby, 2000). Hydrothermal crusts precipitate directly from hydrothermal solutions that are vented in areas with high heat flow associated with hydrothermal fields and submarine volcanism (Glasby, 2000).

The mineralogy and geochemistry of the studied Fe-rich crusts from the Central and Eastern External Subbetic (Betic Cordillera) and Jbel Juimâa Group (Rifian Calcareous Chain) are congruent with a hydrogenetic context. Mn/Fe ratio exceeding 40 is typical of hydrothermal crusts (Usui et al., 1997), but all Fe-rich crusts studied have values below 0.5 similar to recent hydrogenetic ferromanganese nodules (González et al., 2010).

According to Usui et al. (1997) negative Ce anomaly along with a positive Eu anomaly and low ∑REE (<100 ppm) are characteristics of hydrothermal crusts, while a positive Ce anomaly and high ∑REE are characteristics of hydrogenetic crusts. The values of ∑REE in hydrogenetic crusts exceed 1400 ppm (Hein et al., 1997). In the studied Fe-rich crusts ∑REE is from 309 to 2083 ppm, and there is positive Ce anomaly in PAAS-normalized patterns.

The Fe-rich crusts present contents of Ni, Co, and Pb higher than those of hydrothermal crusts in modern oceans (Glasby, 2000). The Fe-rich crusts studied present higher values of Ni, Co and Pb mainly in the case of Central External Subbetic and Jbel Juimâa Group. Nevertheless, in the case of Eastern External Subbetic the ranges of these elements are within hydrothermal values. The identified minerals (goethite, calcite, lithiophorite and cryptomelane) have been described in relation to hydrogenetic origins (Baturin & Dubinchuk, 2011).

In the case of Mn-rich crusts from Jbel Moussa Group, the mineralogy and geochemistry are congruent with a hydrothermal origin (Reolid et al., 2011). Mn/Fe ratio is 96.9, exceeding the boundary value of 40 typical of hydrothermal precipitates (Usui et al., 1997). In addition, the studied Mn-rich crust ∑REE is 11 ppm and there are negative Ce and positive Eu anomalies in PAAS-normalized patterns confirming the hydrothermal origin. High Eu anomalies in the deposits reflect a process of leaching of Eu^{2+} from the host rocks at temperatures above 250 ºC. According to Glasby (2000) the hydrothermal Mn-crusts in modern 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 ppm). The Mn-rich crust studied presents values within the hydrothermal range for these elements (Cu = 201, Ni = 131, Zn = 95, Co = 87, and Pb = 2 ppm). The identified minerals (Ca-birnessite, cryptomelane, and coronadite) have been reported in hydrothermal vent deposits (Glasby et al., 2005; Canet & Prol-Ledesma, 2007).

The comparison between fossil ferromanganese crusts and recent oceanic hydrogenetic and hydrothermal crusts suggests that the geochemical approach is a useful tool for identify the origin but a wide range of geochemical parameters must be employed. The most determinative parameter is the presence of anomalies in REE (Ce and Eu) compared to chondrite and PAAS normalized patterns. In the contrary, contents of Ni, Co, and Pb may be insufficient in some cases and fail to identify hydrogenetic origins (case of samples from Eastern External Prebetic).

ACKNOWLEDGEMENTS

REFERENCES

Baturin, G.N. & Dubinchk, V.T. (2011): Mineralogy and chemistry of ferromanganese crusts from the Atlantic Ocean. Geochemistry International, **49**, 578-593.

Canet, C. & Prol-Ledesma, R.M. (2007): Mineralizing processes at shallow submarine hydrothermal vents: examples from México. GSA Spec. Papers, **422**, 359–376.

Fleet, A.J. (1983): Hydrothermal and hydrogenous ferromanganese deposits: do they from a continuum? The rare evidence. In "Hydrothermal Processes at Seafloor Spreading Centers", P.A. Rona, K. Boström, L. Laubier, Jr.K.L. Smith, eds. Plenum Press, New York, 535–555.

Glasby, G.P. (2000): Manganese: Predominant role of nodules and crusts. In "Marine Geochemistry", H.D. Schultz, M. Zabel, eds. Springer, Heidelberg-New York, 335–372.

–, Papavassiliou, C.T., Mitsis, J., Valsani-Jones, E., Liakopoulos, A., Renner, R.M. (2005): The Vani manganese deposits, Milos island, Greece: A fossil stratabound Mn-Ba-Pb-Zn-As-Sb-W-rich hydrothermal deposit. Development in Volcanology, **7**, 255–291.

González, F.J., Somoza, L., Lunar, R., Martínez-Frias, J., Rubi, J.A.M., Torres, T., Ortiz, J.E., Díaz del Río, V. (2010): Internal features, mineralogy and geochemistry of ferromanganese nodules from the Gulf of Cadiz: The role of the Mediterranean Outflow Water undercurrent. J. Mar. Systems, **80**, 203-218.

Hein, J.R., Koschinsky, A., Halbach, P., Manheim, F.T., Bau, M., Kang, J.K., Lubick, N. (1997): Iron and manganese oxide mineralization in the Pacific. Geol. Soc. Spec. Pub., **119**, 123–138.

Jiménez-Millán, J. & Nieto, L.M. (2008): Geochemical and mineralogical evidence of tectonic and sedimentary factors controlling the origin of ferromanganese crusts associates to stratigraphic discontinuities (Betic Cordilleras, SE of Spain). Chemie der Erde, **68**, 323–336.

McDonough, W.F. & Sun, S.S. (1995): The composition of the Earth. Chemical Geology, **120**, 223–253.

Reolid, M. (2011): Palaeoenvironmental contexts for microbial communities from Fe-Mn crusts of Middle-Upper Jurassic hardgrounds (Betic-Rifian Cordillera). Rev.. Esp. Pal., **26**, 135-160.

–, El Kadiri, K., Abad, I., Olóriz, F., Jiménez-Millán, J. (2011): Jurassic microbial communities in hydrothermal manganese crust from the Rifian Calcareous Chain, Northern Morocco. Sed. Geol., **233**, 159-172.

Taylor, S.R., & McLennan, S.M. (1985): The Continental Crust: its Composition and Evolution, A. Hallam, ed. Blackwell Scientific Publications, Oxford, 151 pp.

Usui, A., Bau, M., Yamazaki, T. (1997): Manganese microchimneys buried in the Central Pacific pelagic sediments: evidence of intraplate water circulation? Mar. Geol., **141**, 269–285.