Revista Mexicana de Ciencias Geológicas, volumen 17, número 2,
2000, p. 143- 153
Universidad Nacional Autónoma de México, Instituto de Geología,
México, D.F

MINERALOGICAL STUDY OF THE LA HUECA CRETACEOUS IRON-MANGANESE DEPOSIT, MICHOACÁN, SOUTHWESTERN MEXICO

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ABSTRACT

In this work we describe for the first time the mineralogy and very briefly the possible origin of a banded Fe-Mn deposit associated with a Cretaceous volcanosedimentary sequence of the southern Guerrero terrane, near the sulfide massive volcanogenic deposit of La Minita. The deposit is confined within a felsic tuff unit; about 10 meters thick where sampled for chemical analysis. Using XRF, EDS and XRD techniques, we found besides todorokite, cryptomelane, quartz, romanechite (psilomelane), birnessite, illite-muscovite, cristobalite, chlorite, barite, halloysite, woodruffite, nacrite or kaolinite, and possibly hollandite-ferrian, as well as an amorphous material and two unknown manganese phases.

Although the manganese and iron minerals that characterize the La Hueca site were apparently somewhat altered by diagenetic or weathering processes, the combined evidence of finely banded to laminated structure, the abundant presence of Fe, Mn, Ba, Zn, and Si, and a mineralogy of probable primary originm here represented by hematite, jasper and manganese minerals enriched in zinc and barium, strongly support the interpretation that La Hueca is essentially of sedimentary origin, precipitated from hydrothermally metal-enriched solutions. The deposit is here interpreted as a distal exhalite derived from the same hydrothermal solutions that formed the barite-sulfides deposits of La Minita.

Key words: Mineralogy, La Hueca iron-manganese deposit, Michoacán, Mexico

RESUMEN

En este trabajo se describe por vez primera la mineralogía y el posible origen de un depósito sedimentario bandeado de Fe-Mn asociado con una secuencia volcanosedimentaria del Cretácico, ubicada en la parte sur del terreno Guerrero, cercano al depósito de sulfuros masivos volcanogénicos de La Minita. El depósito se encuentra dentro de una unidad de tobas félsicas de aproximadamente 10 m de espesor, y consiste de capas finamente bandeadas de jaspe, hematita y manganeso, de donde se obtuvieron muestras para su análisis químico. Utilizando técnicas de XRF, EDS y XRD, se encontró que la todorokita y el cryptomelano son las dos especies principales del manganeso, pero además existen otros dos minerales de manganeso que no fueron identificados. Basado en los resultados obtenidos por XRD, se identificaron los minerales: hematita, todorokita, cryptomelano, cuarzo, romanechita (psilomelano), birnessita, illita-muscovita, cristobalita, clorita, barita, halloysita, woodofrita, caolinita, y posiblemente hollandita férrica, así como un material amorfo y dos fases desconocidas de manganeso.

Aunque los minerales de manganeso y hierro que caracterizan al prospecto de La Hueca están aparentemente alterados por procesos diagenéticos o de intemperismo, la evidencia combinada de una estructura laminar, finamente bandeada, la gran abundancia de Fe, Mn, Ba, Zn y Si, y una mineralogía de posible origen primario representada por hematita y jaspe, así como minerales de manganeso enriquecidos en zinc y bario, apoyan fuertemente la interpretación de que los yacimientos de hierro de La Hueca son de origen sedimentario, precipitados a partir de soluciones enriquecidas hidrotermalmente. El yacimiento se ha interpreatdo en este trabajo como un depósito distal, derivado de las mismas soluciones hidrotermales que formaron al depósito de sulfuros masivos de La Minita.

Palabras clave: Mineralogía, depósito de hierro-manganeso de La Hueca, Michoacán, Mexico

INTRODUCTION

The purpose of this work is to describe the mineralogy and geochemistry of ironstone hosted in Cretaceous volcanosedimentary rocks of the Guerrero-Colima orogenic belt. Only few sedimentary Fe and Mn oxides associated with

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cryptocrystalline silica have been described in Mexico: La Prosperidad, in Baja California (Jacobson, 1982), and San Francisco, in Autlán, Jalisco (Zantop, 1978; 1981).

This newly described deposit is known as the La Hueca mine, or Sapo Negro (Ortigosa-Cruz et al., 1994, and Miranda-Gasca, 1995). It is situated in northwestern Michoacán, municipality of Coalcomám, 4 km east of La Minita volcanogenic sulfide deposit (Gaitán-Rueda et al., 1979) (Figure 1). Although the La Hueca mine prospect has been known as part of the La Minita Mining District for more than a century, its character as a sedimentary one was first suggested very recently (Ortigosa-Cruz et al., 1994).

However, no studies on the metallogenic, geochemical or mineralogical conditions for the deposit had been done.

GEOLOGICAL SETTING

La Hueca sedimentary ironstone is located in the southern part of the Guerrero terrane, in the Zihuatanejo subterrane (Campa and Coney, 1983). The stratigraphic column correspondsd with more than 2,000 m thick. Submarine andesites and rhyolitic tuffs are interbedded with shales, graywackes, and limestones locally known as Tecalitlán Formation (Rodríguez, 1980; Pantoja-Alor and Estrada-Barraza, 1986) and Tepalcatepetl Formation (Pimentel, 1980). It is important to note that in the vicinity of the La Hueca iron deposit, no evidence of igneous intrusions is found, such as those which are common in the iron deposits of Peña Colorada, Cerro Náhuatl and EI Encino, located in the same tectonostratigraphic terrane. Thus, the iron mineralization at la Hueca can not be related to any magmatic intrusion.

La Hueca deposit occurs within a distinctive sequence of felsic tuffs at the lower part of Cerro de Las Minas. The Cretaceous volcanosedimentary rocks were folded during the Laramide Orogeny, with the La Hueca deposit located on the western flank of an anticline of that age, oriented WNW-ESE.

LOCAL STRATIGRAPHY

A 10 m thick section of pyroclastic rocks in the Tecalitlán or Tepalcatepetl Formation that contains the ironstone was sampled, because it contains the best expression of the banded structure of the deposit. The outcrop consists of rhyolitic tuffs interbedded with jasperoids, containing the finely banded layers enriched in Fe, Mn, Zn, and Ba (Figures 2 and 3). The sequence was divided into 7 members or intervals:

•1. Black, manganiferous sedimentary bed,
•2. Laminated tuff,
•3. Manganiferous tuff,
•4. Soft banded hematite-jasper bed,
•5. "Hard" banded hematite-jasper bed,
•6. Banded hematite bed, and
•7. Banded hematite with laminated tuff. The unit occurs in the middle portion of a 1,000 m thick sequence. Andesitic breccias

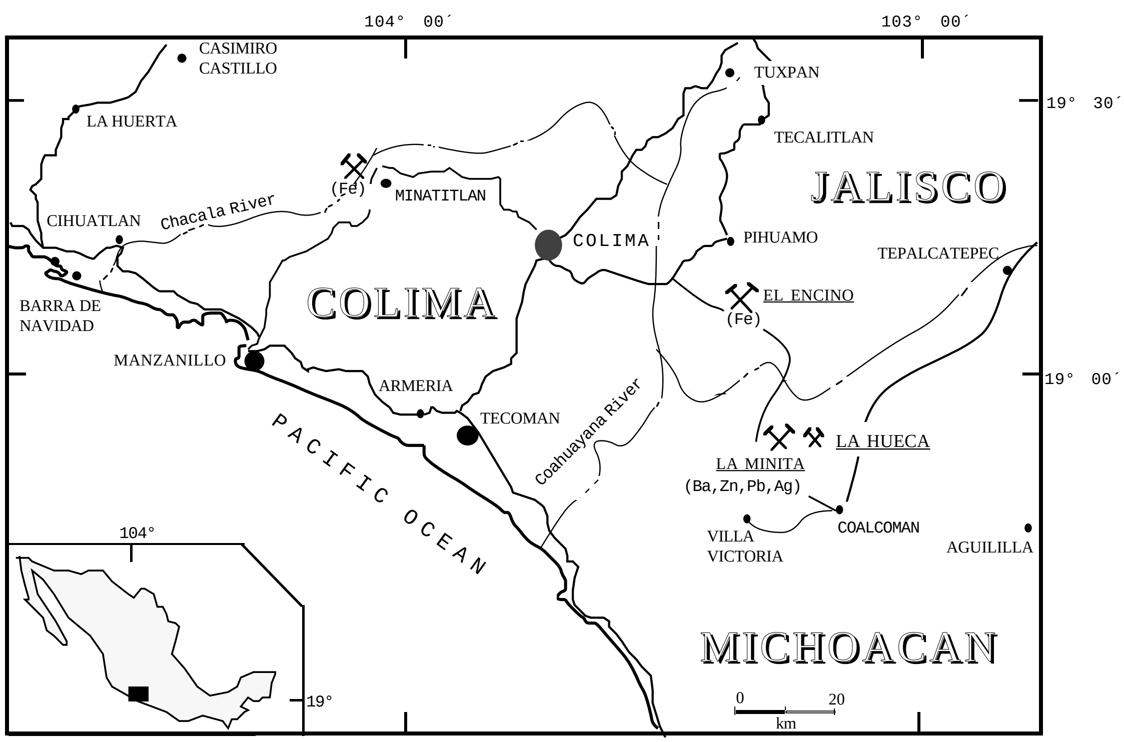


Figure 1. Location map of the La Hueca deposit area.

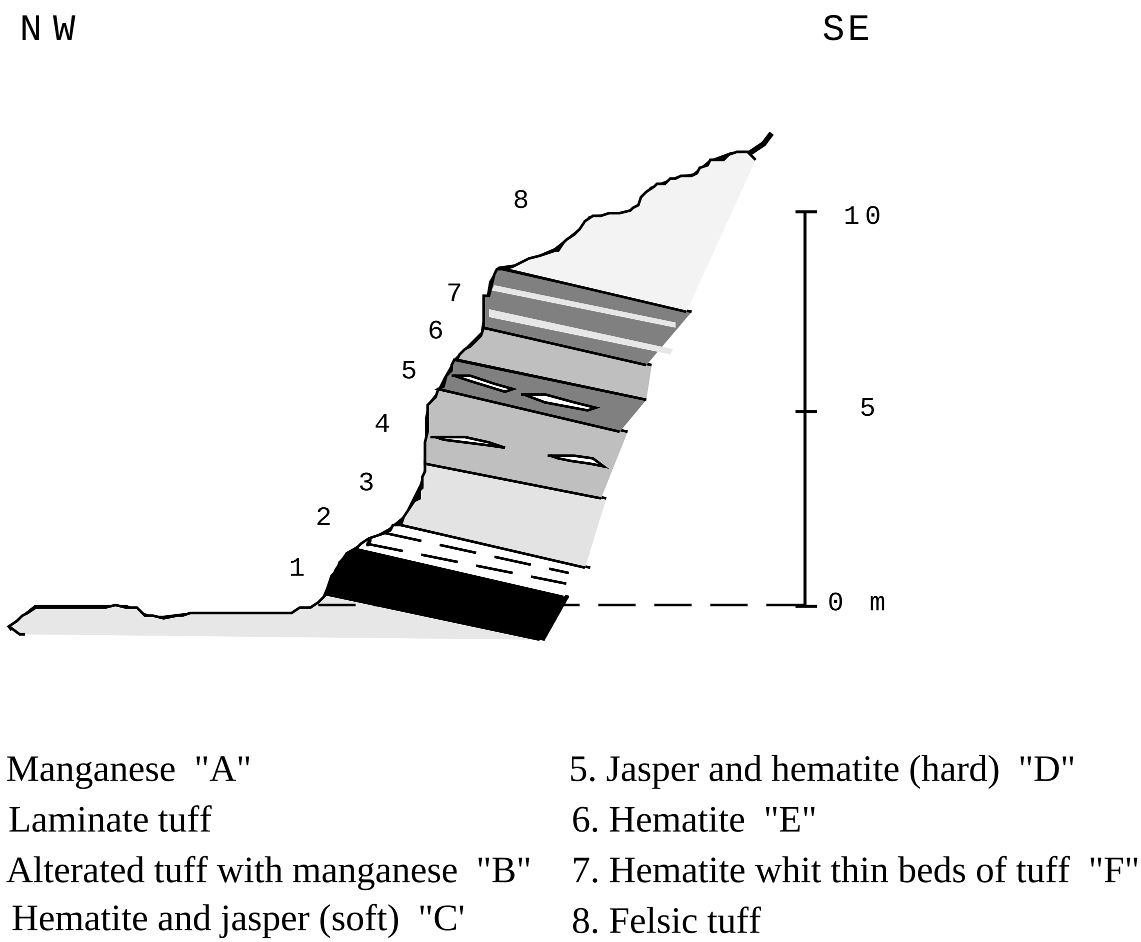


Figure 2. Stratigraphic section of the La Hueca Fe-Mn deposit.

Figure 3. Figure 3. Hematite and jasper beds of the La Hueca Fe-Mn deposit.

are present at its lower part, while gray shales interbedded with felsic tuffs and scarce; fossiliferous limestones are common at its upper portion (Figure 4). The sequence dips 40° to the southwest, and is placed in the flank of a NW-trending anticline.

MINERALOGY

PETROGRAPHY

Unit 1. Manganese “A”. This unit forms the base of the sequence and is composed by a layer with dusty texture, black color and 1 meter thick. Under the microscope it shows a very fine granular texture, formed by manganese and hematitic oxides, with disseminated subhedral crystals of altered plagioclase. The friable state of this rock prevented its further petographic description because textures in thin section are very porous and mechanically dispersed.

Unit 2. Laminated tuff. It corresponds to a felsic tuff 0.50 m thick without minerals of Fe or Mn. No thin section was cut from this rock.

Unit 3. Altered tuff with manganese “B”. It corresponds to a band 1.80 m thick formed by a felsic, very altered tuff , which contains disseminated manganese oxides. In thin section it consists of very abundant and completely altered (kaolinized?) plagioclase pseudomorphs set in a connected matrix of opaque hydroxides and altered rare flakes of a micaceous mineral. Incipient sericite is forming from the clay mineral that forms the plagioclase pseudomorphs. The rock was probably a plagioclase crystal tuff.

Unit 4. Hematite and jasper (soft) “C”. This unit is constituted by a packet 2 m thick of hematite thin beds with interbedded lens-shaped bodies of jasper. In thin section the hematitic part consists of massive aggregates of sub-microscopic reddish hematite dust.

Unit 5. Jasper and hematite (hard) “D”. This interval is composed of submillimetric laminations distributed in bands of different mineral composition, ranging in color from dark to dark reddish and light shades (thin section 944D). The darker material is also the most finely-laminated, and granular quartz and platy transparent to semiopaque bright red hematite form it. The plates of hematite show a random orientation with intersertal texture. Quartz forms a mosaic of unstrained crystals but affected by multiple fractures. Quartz and a dispersed scarce clay mineral form the light bands. Quartz

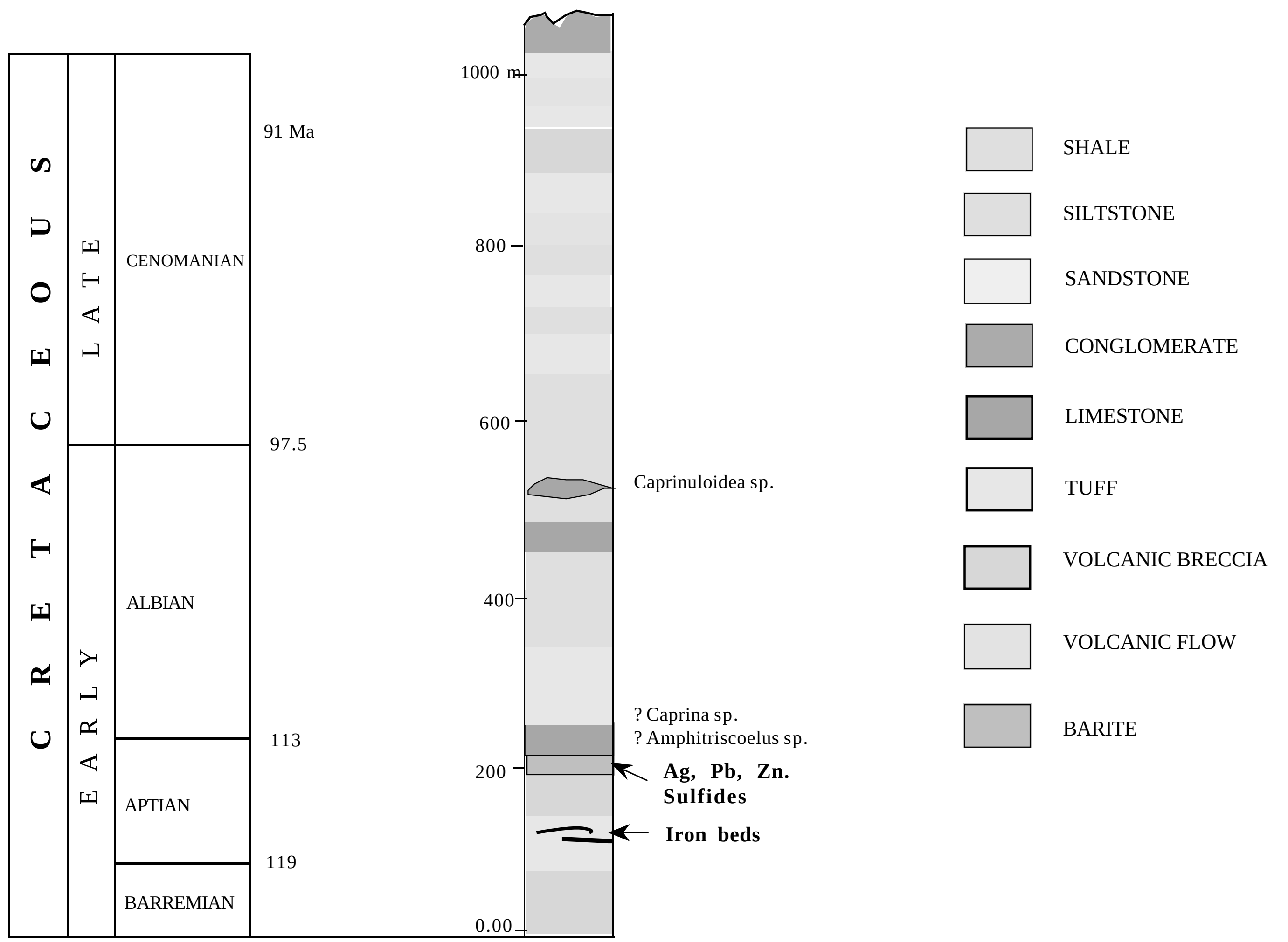


Figure 4. Stratigraphic column of the La Minita-La Hueca area.

forms an aggregate of multiple grains with lobated to slightly curved intergranular contacts. Grain size varies from an average of about 70 µm in the least recrystallized areas, up to nearly 1 mm in the most recrystallized zones. These bands have an irregular shape, from 2 to about 0.5 mm. Next to this band, an almost opaque zone is formed by hematite as a massive aggregate of plates and a little quartz including several patches of chert.

The light red bands are formed by hematite finely disseminated on microcrystalline quartz with abundant equal-angle triple junctions and straight boundaries. Microfractures across these bands are filled with secondary quartz. Grain size of quartz, in this case, is about 50 µm, whereas the hematite is 1-3 µm. The darker red bands have the same characteristics, but hematite is more abundant and forms opaque massive zones by coalescence of the crystalline fine grains. Secondary features include quartz-filled microveins perpendicular to the lamination, along which some hematite was remobilized. These veins may coalesce in wider but irregular zones in which grain size increases from 45-90 µm on the margins, to about 0.5 mm in the central areas.

994 D" Interval 6. Jasper and hematite (hard) "D". This rock in thin section is similar to 944 D, but laminated-banded structure is flatter and contains abundant cross-cutting, irregular veins and patches of crystalline quartz. It also shows a brown, dull, massive phase intimately intergrown with crystalline hematite in the hematite-rich bands.

R 53 A Interval 7. Hematite whit thin beds of tuff "F". This rock consist of an irregularly hematite-rich banded structure with lens-shaped areas formed by a cryptocrystalline quartz matrix with abundant iron-rich chlorite (chamosite?) and submicroscopic iron oxide dust, possibly hematite. The chlorite occurs dispersed in the silicic matrix and forming oval inclusions about 100 µm on the long dimension. The dark zones consist of massive hematite with regularly distributed lens-shaped zones of material forming the quartz-chlorite bands and patches. Both types of bands grade into each other. The internal structure of the chloritic bands shows a distinct preferred orientation of the mica. A brown, highly birrefringent phyllosilicate rimming a group of chlorite flakes in a few of the oval inclusions was tentatively identified as stilpnomelane.

ANALYTICAL TECHNIQUES

The rocks collected in the outcrops described above were studied in the geochemical laboratories of the Instituto de Geología of the Universidad Nacional Autónoma de México (LUGIS), by X-ray fluorescence spectrometry, and X-ray diffraction techniques, in order to determine the composition, mineralogy, and the geochemistry of silicates and Fe and Mn oxides that form the metaliferous deposit. The samples were also analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray microanalyser (EDX) attached to a JEOL jsm 35 c instrument. Operating conditions were set at 15 kV accelerating voltage and 100 second measuring time. In addition, X-ray diffraction (XRD) analyses were performed on some samples using a Philips pw 1050/25 diffractometer with graphite monochromatic. X-ray fluorescence spectrometry (XRF) analyses were performed on isolated todorokite using a Siemens SRS 3000 X-ray spectrometer with Rh target. Experimental profiles were analyzed using Siemens Semi Quant software.

DESCRIPTIVE MINERALOGY

Based on the results obtained by XRD, the following minerals were identified (Table 1): Hematite, todorokite, cryptomelane, quartz, romanechite (psilomelane), birnessite, illite-muscovite, cristobalite, chlorite, barite, hollandite-ferrian?, halloysite, woodruffite, nacrite or kaolinite, as well as an amorphous material and two unknown manganese phases.

These minerals were analyzed by SEM (EDS) to determine their wt % major oxide contents (Table 2). We also found many other manganese minerals such as bixbyite, coronadite, rhodonite, and ottrelite, which could not be identified using XRD. The identification was based on their major element content, in some cases confirmed by XRD studies and in others by their specific crystal shapes.

Conspicuous radial and ooidal structures were observed of about 100 µm to 1 mm, that are formed mainly of hematite and alteration products rich in silica (sample 6-E, Plate 1, b).

Complementary trace element analyses were obtained from representative samples of each bed of the La Hueca deposit, and two from the volcanogenic sulfide deposit of La Minita (Table 3).

Todorokite. This mineral contains 8.3 wt % of ZnO. Todorokite of Phillipsburg, Montana, contains 5% Zn (Larson, 1962). Barium content is also higher (5.30 wt% BaO). Todorokite crystals are less than 1 µm in diameter and it is intergrown with an unidentified manganese silicate and clay minerals. Other phases of similar composition but of botroidal, radial, and tubular shape, are associated to todorokite. These phases are larger than todorokite, from 50 to 200 µm (samples 1 A and 3 B, Plate 1, c and d; and Table 2).

Cryptomelane. The chemical composition obtained using EDX on this phase identifies a typical cryptomelane (Table 2). It occurs in small needle-like prismatic crystals less than one micron in size, and is intergrown with quartz in drusses (sample 1-A, Plate 2, a). It is present also as a cryptocrystalline mineral, collomorphic to radial in shape, and with botryoidal and concentric structures.

Unknown manganese silicates. Two manganese silicate minerals were identified:

•1. A botryoidal, tubular phase, 10-100 µm long, that contains more than 30 wt % iron oxide and,

•2. A long and radial mineral with about 20 wt % iron oxide (Table 2 and Plate 2, c). They are however scarce (sample 3B).

Albite. It is present in the sedimentary part of interval 3. This plagioclase is scarce, with only two crystals observed, both

Table 1. Minerals identified by XRD in each unit of the La Hueca deposit.

UNIT	SAMPLE	IDENTIFIED MINERALS	FORMULA COMPOSITION
1. Manganese	H1-1	Romanechite	$(Ba,H_2O)(Mn^{4+},Mn^{3+})_5O_{10}$
	H1-2	Quartz	SiO_2
		Woodruffite?	$(Zn,Mn^{2+})Mn_3O_7 \cdot 1\text{-}2H_2O$
3. Alterated tuffs with manganese	H3-1	Feldspar	$M,Al(Al,Si)Si_2O_8$ M= K,Na,Ca,Ba
	H3-2	Barite	$BaSO_4$
		Romanechite	$(Ba,H_2O)(Mn^{4+},Mn^{3+})_5O_{10}$
		Halloysite?	$Al_2Si_2O_5(OH)_4$
		Quartz	SiO_2
		Cryptomelane	$K(Mn^{4+}, Mn^{2+})_8O_{16}$
		Illite-muscovite?	$(K,H_3O)(Al,Mg,Fe)_2(Al,Si)_4O_{10} \cdot OH_2,H_2O$
4. Hematite and jasper (soft)	H4-1	Hematite	Fe_2O_3
	H4-2	Quartz	SiO_2
		Chlorites	$M_{5\text{-}6}(Al,Si)_4O_{10}(OH)_8$ M= Mg,Fe,Ni,Mn,
5. Jasper and hematite (hard)	H5-1	Quartz	SiO_2
	H5”1	Hematite	Fe_2O_3
	H5-2	Romanechite	$(Ba,H_2O)(Mn^{4+},Mn^{3+})_5O_{10}$
	H5-3	Todorokite	$(Mn^{2+},Ca,Mg)Mn_3O_7 \cdot H_2O$
	H5-4	Birnessite?	$Na_4Mn_{14}O_{27} \cdot 9H_2O$
		Hollandite-ferrian?	$Ba(Mn^{4+},Mn^{2+})_8O_{16}$
		Barite	$BaSO_4$
6. Hematite	H6-1	Quartz	SiO_2
	H6-2	Hematite	Fe_2O_3
		Woodruffite	$(Zn,Mn^{2+})Mn_3O_7. 1\text{-}2H_2O$
		Romanechite?	$(Ba,H_2O)(Mn^{4+},Mn^{3+})_5O_{10}$

Plate 1. Scanning electron photomicrographs. a) Sample 5D: 1. jasper, 2. barite, 3. hematite. b) Sample 6E; ooidal structures. c) and b) Sample 1A; manganese minerals.

euhedral and 60 to 80 µm in size, with their surfaces corroded and altered to clay (sample 3 B). Its measured composition is Ab_{98}, and could be of diagenetic origin.

K-Feldspar (sample 3B). It is present but rare. The crystals are tabular, subhedral, and varying in size from 40 to 60 µm, with altered margins and holes affecting their surfaces. The specific nature of this phase was not identified.

Barite. This mineral is stratiform and is interbedded with hematite and jasper (sample 5 D Plate 1, a). It is present as euhedral crystals and intergrown with hematite and jasper in intervals 5 and 6.

Zinc-barium-manganese mineral of radial habit (Woodruffite?). This mineral is present in amounts less than 10%. It contains about 17% of ZnO and 5 wt % of BaO (Table 2) and exhibits a well developed radial pattern. The radial masses reach up to 300 µm in length and are composed of many long (20 µm) and very thin leaves (Sample 3 B, Plate 2, b).

Iron-manganese mineral (Bixbyite?) (Sample 3B, 4C). This mineral forms rectangular bodies about 8 to 12 µm thick.

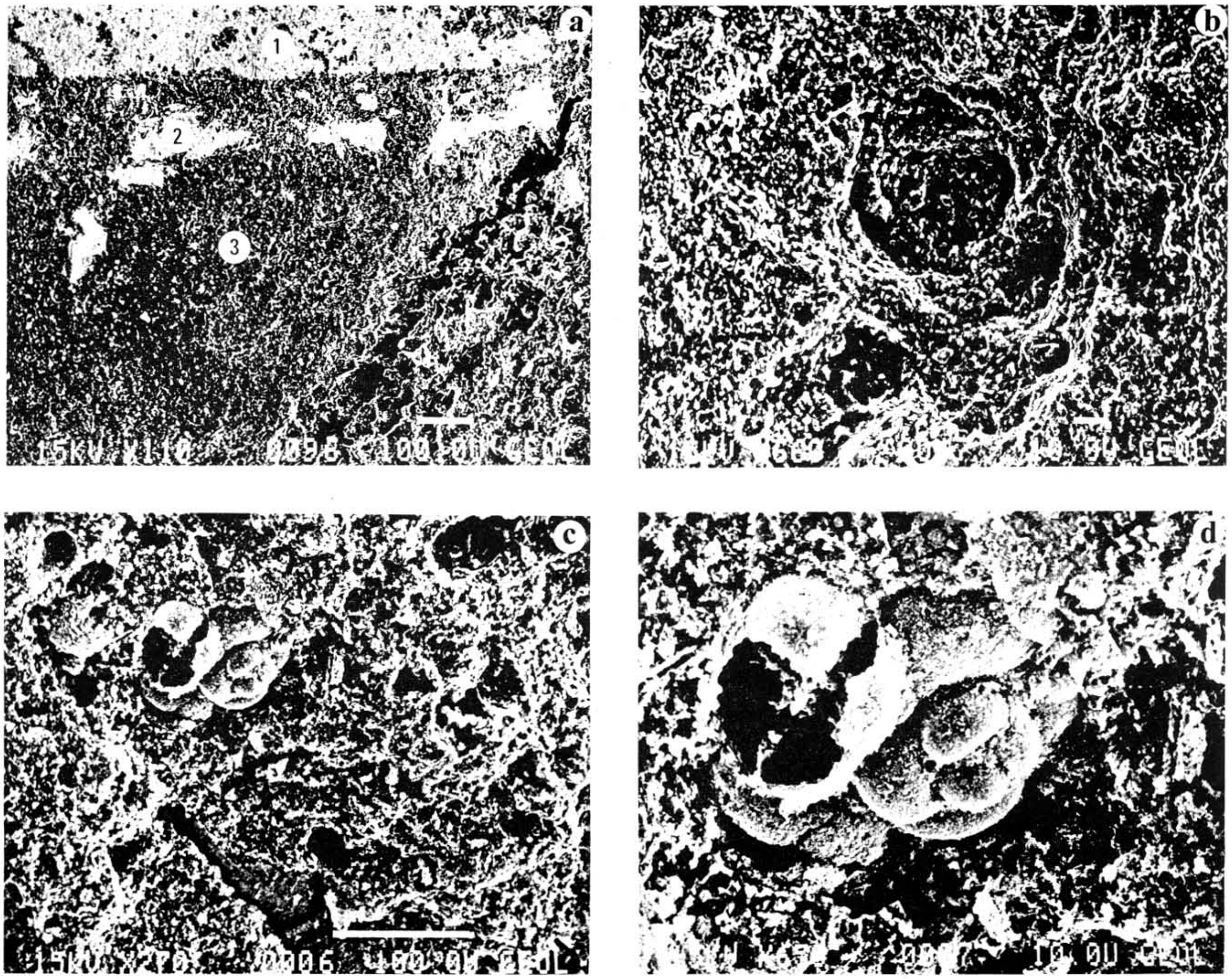
Iron-manganese mineral of radial form (sample 3B, 4C). Commonly occurs as botryoidal masses of very fine acicular crystals in concentric and radial layers.

Psilomelane (sample 5 D). It is observed in small needle-like prismatic crystals (>1 µm), often intergrown with todorokite.

Quartz in druses (sample 3B, Plate 2, d). Occurs as euhedral crystals and as aggregates, often associated with barite and romanechite. It is observed in vein too; as crystal masses of 3-5 µm, and as crystal masses of 40-50 µm.

CLOSING COMMENTS

Relationships of Fe/Mn, Cu+Ni+Co, and formation processes of Fe-Mn deposits are illustrated schematically in Figure 5, where it can be seen that all samples from the La Hueca deposit fall in the hydrothermal field, precluding the possibility of a substantial late diagenetic or hydrogenetic



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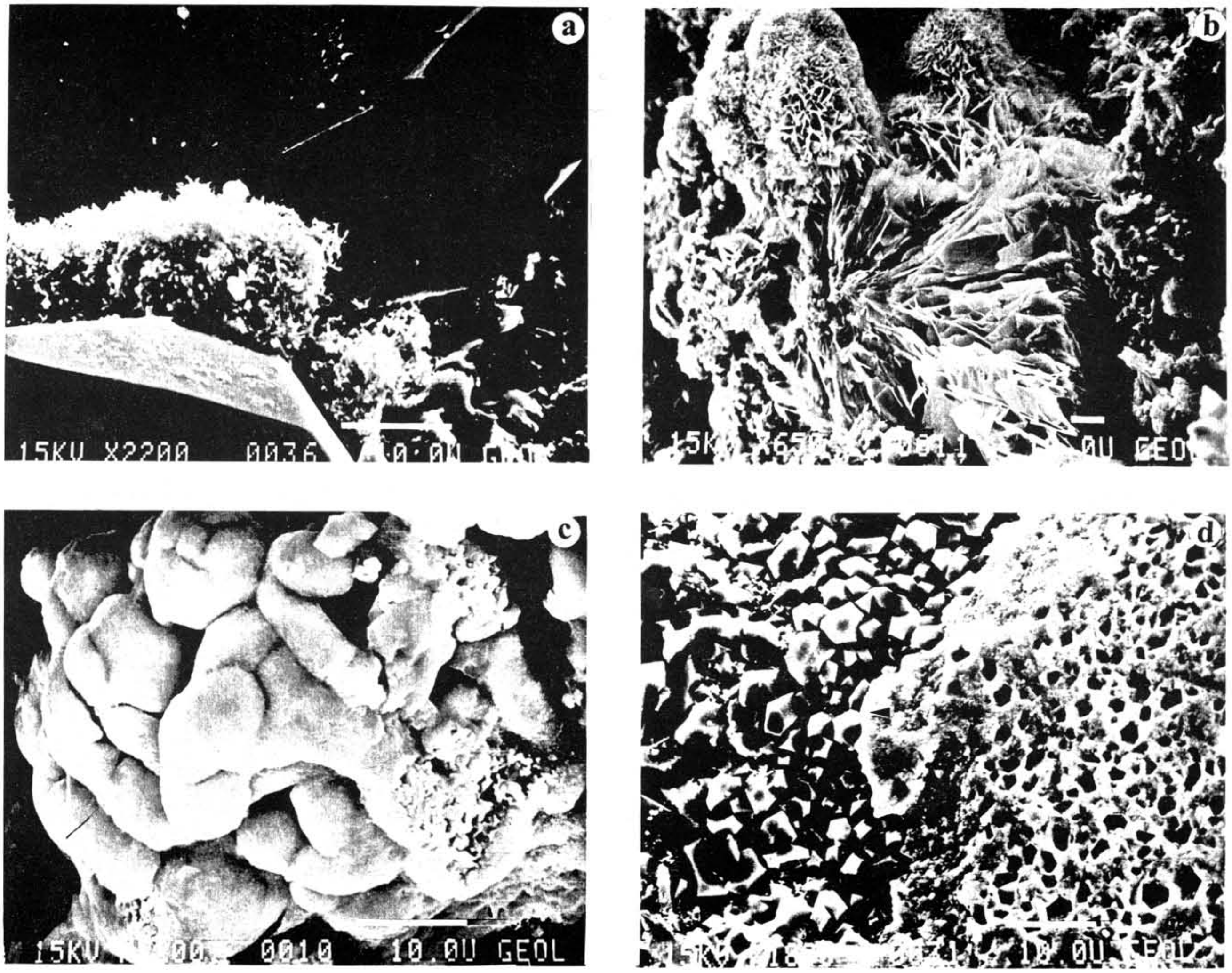

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Hueca deposit fall in the hydrothermal field, precluding the possibility of a substantial late diagenetic or hydrogenetic enrichment. On the other hand, the high Si/Al ratios (more than 3 for intervals 1, 4, 5 y 6), indicate that the origin of the deposit is related to hydrothermal fluids that precipitated in a subaqueous environment (Bonatti *et al.*, 1972b).

In general, mineral concentrations of the La Hueca deposit are similar to present precipitates of Mn and Fe related to hot springs, and to the concentrations in old Mn deposits of volcanosedimentary origin, with the only difference that in the La Hueca deposit concentrations of Ba and Zn are much higher, and those of Cr, Ni, and Co much lower (Table 3).

The two main manganese minerals, cryptomelane and todorokite, present in the La Hueca iron deposit, are common in stratiform Fe-Mn deposits of the world (Frenzel, 1980). They are secondary alteration products of other primary manganese minerals, such as manganese carbonates, hausmannite, braunite (apparently present at the La Hueca deposit), and rhodonite.

Although the manganese and iron minerals that characterize the La Hueca site were apparently somewhat altered by diagenetic or weathering processes, the combined evidence of finely banded to laminated structure, the abundant presence of Fe, Mn, Ba, Zn, and Si, and a mineralogy of probable primary origin, here represented by hematite, jasper and manganese minerals enriched in zinc and barium, strongly support the interpretation that the La Hueca ironstone is essentially of sedimentary origin (chemically or biochemically precipitated from hydrothermally metal-enriched solutions). It is considered to be related to the nearby La Minita volcanogenic massive sulfide deposit. Both can be stratigraphically correlated and occur only about 4 km away from each other. This type of Fe-Mn stratiform deposit

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Table 2.- Quantitative microprobe analysis (wt%) (ED) of minerals identified in each horizon

	RHODONITE ?	RHODONITE ?	BIXBYTE	BIXBYTE	CORONADITE	HEMATITE	BARITE W/ Fe, Zn.	JASPER	JASPER
	Unit:1 Sample: H1 Nº analysis: (5)	Unit: 3 Sample H 3 Nº analysis (5)	Unit: 3 Sample: H 3 Nº analysis: (4)	Unit:4 Sample: H 4 Nº analysis: (5)	Unit: 5 Sample: H 5-1 Nº analysis: (5)	Unit: 5 Sample: H 5-3 Nº analysis: (5)	Unit: 5 Sample: H 5-3 Nº analysis: (5)	Unit: 5 Sample: H 5-3 Nº analysis: (5)	Unit: 5 H5''2 (5)
SiO_2	37.53	29.79	6.35	7.85				63.69	86.8
TiO2	0.26	0.41	0.41	0.23					
Al_2O_3	4.58	18.86	7.85	1.82					
FeO	4.04	8.99	18.02	41.26	0.84	80.26	12.08	11.7	7.88
MgO	1.43	2.14	1.26	0.82					
MnO	39.68	23.6	48.65	35.43	63.27	6.71	0.38	13.8	0.08
CaO	0.48	0.11	0.09	0.32					
Na_2O	1.19	1.29	1.44	1.01					
K_2O	1.28	3.32	0.71	0.23					
BaO	0.11	4.48	7.31	2.97	13.75	0.65	48.88	5.97	0.08
ZnO	0.72	3.62	4.12	3.95	2.22	1.1	35.05	3.72	2.07
CuO			3.77	4.09	7.04	3.3	0.99	0.86	3.03
PbO						6.17	1.59		

	OTTRELITE	BIXBYTE	Fe, Al SILICATE	WOODROFFITE	TODOROKITE	CRYPTOMELANE	WOODROFFITE	Fe-Mn	PSILOMELANE
	Unit: 5 Sample: H 5''- 4 Nº analysis: (6)	Unit: 6 Sample: H 6-1 Nº analysis: (5)	Unit: 6 Sample: H 6-2 Nº analysis: (6)	Unit: 6 Sample: H 6-2 Nº analysis: (6)	Unit: Sample: 1-A Nº analysis: (3)	Unit: 6 Sample: 1-A, 6E Nº analysis: (4)	Unit: 3 Sample: 3B Nº analysis: (2)	Unit: Sample: 3B, 4C Nº analysis: (7)	Unit: Sample: 5D Nº analysis: (3)
SiO_2	29.19	8.02	39.98	5.7	2.71	0.51	1.01	1.47	5.48
TiO_2		0.23	0.17	0.31					
Al_2O_3		4.33	16.54	5.86	1.57	1.62		3.41	2.38
FeO	57.32	45.38	38.93	4.14	5.71	7.22	0.78	24.34	1.89
MgO		0.95	1.27	2.49					
MnO	8.41	36.16	2.06	70.38	75.25	84.87	69.20	58.66	67.24
CaO		0.09	0.02	0.26					
Na_2O		0.73	0.40	2.37					
K_2O		0.5	0.18	1.63	1.15	1.89	0.07	0.07	0.16
BaO	4.87				5.30	1.32	5.30	4.4	18.23
ZnO	0.07	2.58	1.18	4.38	8.30	4.13	17.35	5.27	1.39
CuO	0.13	3.05	1.88	2.45					
PbO									

Table 3. Trace elements of samples at La Minita and horizons at the La Hueca deposits.

	LA MINITA		LA HUECA					
ELEMENTOS	9419	947	944A	944B	944C	944D	53B	944E
	Pb/Zn	Pb/Zn	Mn	tuff/Mn	hem/jasp	jasp/hem	Jasp/hem	hem
Ba	*	*	118	*	*	*	*	1616
Co	442	107	85	9	< 3	< 3	< 3	< 3
Cr	3	4	31	15	59	54	14	79
Cu	< 0.7	120	< 0.7	71	25	< 0.7	51	24
Nb	2	2	3	11	2	2	2	3
Ni	14	17	147	56	70	3	< 0.5	309
Rb	8	6	26	109	4	4	5	10
Sr	1532	833	231	32	69	466	1178	105
V	90	< 0.5	429	146	< 0.5	496	86	50
Y	< 0.5	< 0.5	< 0.5	14	1	< 0.5	< 0.5	6
Zn	*	*	*	*	593	295	141	*
Ga	< 0.9	< 0.9	< 0.9	9	6	5	3	8
Zr	73	47	46	189	16	30	60	32

* Extremely high values

derived from the same hydrothermal solutions that precipitated sulfides as they reached the seawater-rock interface (Franklin, et al., 1981).

The La Hueca Fe-Mn deposit is here interpreted as a distal exhalite derived from the same hydrothermal solutions that formed the barite-sulfides deposits of La Minita. The mineralogy and extremely rare occurrence of oolitic texture at the La Hueca deposit, preclude its classification as an ooidal ironstone, which is typical of other Phanerozoic shallow-water sedimentary environments in which little sediment entered the basin (Young, 1989). The La Hueca Fe-Mn deposit cannot be considered as a sedex type because volcanic rocks of an island arc host it and not sedimentary rocks deposited in intracratonic rifts.

ACKNOWLEDGMENTS

This project was supported by the Consejo Nacional de Ciencia y Tecnología (CONACYT), grant 1318-T9206, and the Instituto de Geología of the Universidad Nacional Autónoma de México (UNAM). We are sincerely grateful to Professors Spencer R. Titley, Half Zantop and Jordi Tritlla for constructively reviewing the manuscript. All remaining flaws should be our sole responsibility. Patricia Altuzar and Leticia Baños worked out the XRD samples and Juan Tomás Vázquez made the thin sections for petrographic and microprobe analyses. We are grateful for their kind help.

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Manuscript received:
Revised manuscript received:
Manuscript accepted:

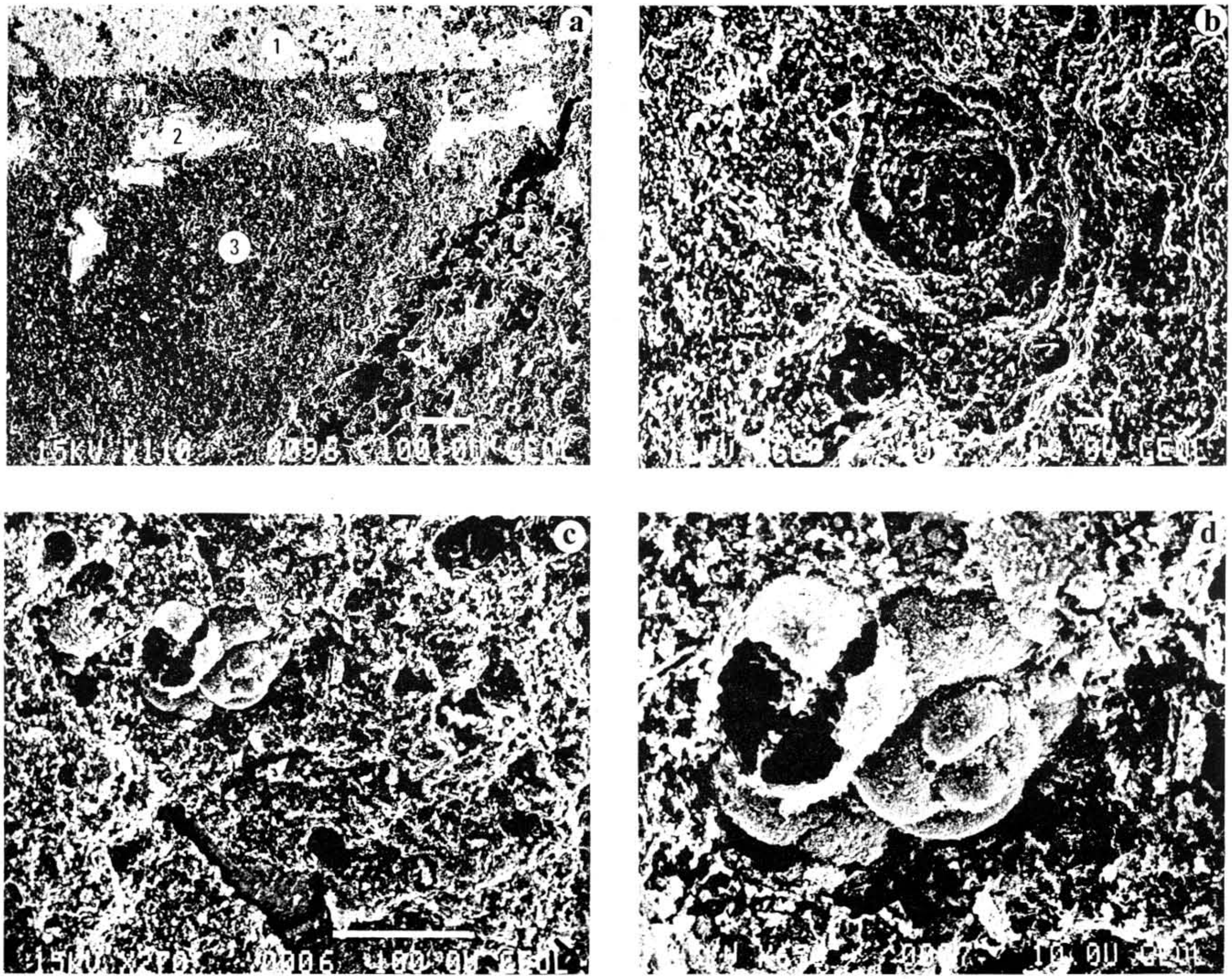

Plate 1. Scanning electron photomicrographs. a) Sample 5D: 1. jasper, 2. barite, 3. hematite. b) Sample 6E; ooidal structures. c) and b) Sample 1A; manganese minerals.

euhedral and 60 to 80 µm in size, with their surfaces corroded and altered to clay (sample 3 B). Its measured composition is Ab_{98}, and could be of diagenetic origin.

K-Feldspar (sample 3B). It is present but rare. The crystals are tabular, subhedral, and varying in size from 40 to 60 µm, with altered margins and holes affecting their surfaces. The specific nature of this phase was not identified.

Barite. This mineral is stratiform and is interbedded with hematite and jasper (sample 5 D Plate 1, a). It is present as euhedral crystals and intergrown with hematite and jasper in intervals 5 and 6.

Zinc-barium-manganese mineral of radial habit (Woodruffite?). This mineral is present in amounts less than 10%. It contains about 17% of ZnO and 5 wt % of BaO (Table 2) and exhibits a well developed radial pattern. The radial masses reach up to 300 µm in length and are composed of many long (20 µm) and very thin leaves (Sample 3 B, Plate 2, b).

Iron-manganese mineral (Bixbyite?) (Sample 3B, 4C). This mineral forms rectangular bodies about 8 to 12 µm thick.

Iron-manganese mineral of radial form (sample 3B, 4C). Commonly occurs as botryoidal masses of very fine acicular crystals in concentric and radial layers.

Psilomelane (sample 5 D). It is observed in small needle-like prismatic crystals (>1 µm), often intergrown with todorokite.

Quartz in druses (sample 3B, Plate 2, d). Occurs as euhedral crystals and as aggregates, often associated with barite and romanechite. It is observed in vein too; as crystal masses of 3-5 µm, and as crystal masses of 40-50 µm.

CLOSING COMMENTS

Relationships of Fe/Mn, Cu+Ni+Co, and formation processes of Fe-Mn deposits are illustrated schematically in Figure 5, where it can be seen that all samples from the La

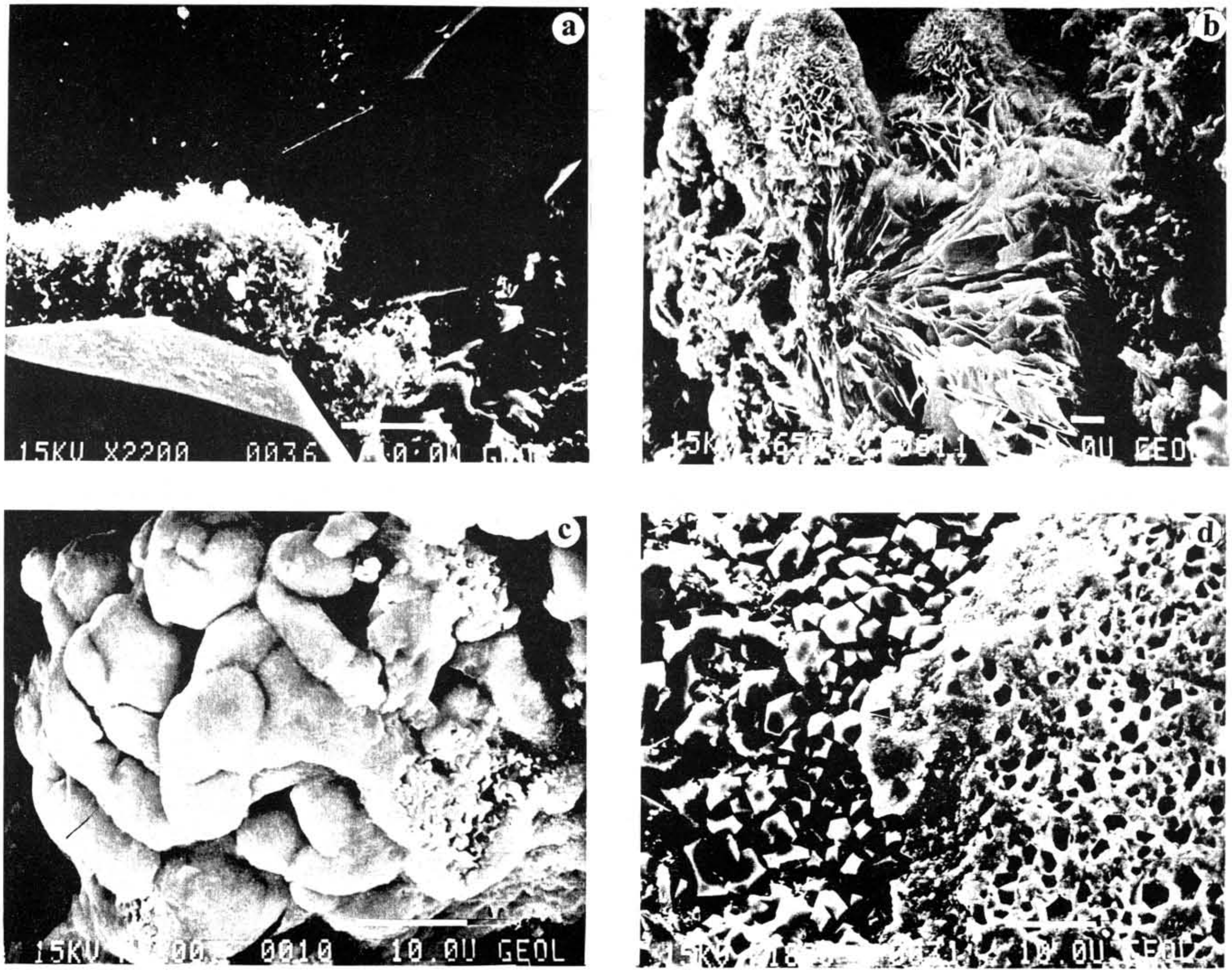

Plate 2. Scanning electron photomicrographs. a) Sample 5D: quartz druse with psilomelane. b) Sample 3B; mineral of manganese with 18% zinc, arranged in radial groups. c) Sample 3B, quartz in druses.

Hueca deposit fall in the hydrothermal field, precluding the possibility of a substantial late diagenetic or hydrogenetic enrichment. On the other hand, the high Si/Al ratios (more than 3 for intervals 1, 4, 5 y 6), indicate that the origin of the deposit is related to hydrothermal fluids that precipitated in a subaqueous environment (Bonatti *et al.*, 1972b).

In general, mineral concentrations of the La Hueca deposit are similar to present precipitates of Mn and Fe related to hot springs, and to the concentrations in old Mn deposits of volcanosedimentary origin, with the only difference that in the La Hueca deposit concentrations of Ba and Zn are much higher, and those of Cr, Ni, and Co much lower (Table 3).

The two main manganese minerals, cryptomelane and todorokite, present in the La Hueca iron deposit, are common in stratiform Fe-Mn deposits of the world (Frenzel, 1980). They are secondary alteration products of other primary manganese minerals, such as manganese carbonates, hausmannite, braunite (apparently present at the La Hueca deposit), and rhodonite.

Although the manganese and iron minerals that characterize the La Hueca site were apparently somewhat altered by diagenetic or weathering processes, the combined evidence of finely banded to laminated structure, the abundant presence of Fe, Mn, Ba, Zn, and Si, and a mineralogy of probable primary origin, here represented by hematite, jasper and manganese minerals enriched in zinc and barium, strongly support the interpretation that the La Hueca ironstone is essentially of sedimentary origin (chemically or biochemically precipitated from hydrothermally metal-enriched solutions). It is considered to be related to the nearby La Minita volcanogenic massive sulfide deposit. Both can be stratigraphically correlated and occur only about 4 km away from each other. This type of Fe-Mn stratiform deposit