

## FERROMANGANESE DEPOSITS IN THE CAVES OF THE GUADALUPE MOUNTAINS

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**ABSTRACT.**—Cave ferromanganese deposits are an unusual type of mineral deposit present in some caves of the Guadalupe Mountains, NM. These deposits consist of several horizons: a layer of soft, altered “punk rock” underneath a highly colored layer, composed predominantly of Fe, Mn, and Al oxides and hydroxides. The deposits contain a diverse microbial community, and DNA analyses indicate that some identified organisms are closely related to known manganese and iron oxidizers. Originally thought to be derived from chemical corrosion of the cave bedrock, the enrichment of Fe and Mn in these deposits cannot be explained solely by the dissolution of carbonate; Fe and Mn are likely transported from the punk rock zone and enriched in the oxide layer. The accumulation of oxides in one horizon, the breakdown of bedrock in another horizon, and the presence of a microbial community suggests that the deposits are similar to soils and may undergo similar processes.

### INTRODUCTION

Accumulations of colorful low density, soil-like material coat the walls, floors and ceilings of several caves in the Guadalupe Mountains, NM. The most abundant deposits are found in Lechuguilla and Spider Caves and occur in a spectrum of color from light pink, to blood red, brick red, ocher, brown, chocolate brown and jet black. They consist of several layers: the outer-most colored layer is mm to cm in thickness and beneath that, a layer of soft, altered bedrock is usually present (Fig. 1). This under layer, called “punk rock” by Hill (1987), occurs in shades of pink, yellow or white and may extend many cm into the wall, eventually grading into hard, unaltered carbonate bedrock. The colored deposits are diverse in composition with variable amounts of clay, quartz, and Al-oxyhydroxide minerals and all are rich in Mn- and Fe-oxides. In general, they can be called ferromanganese deposits (*FMD*), a term that describes accumulations of Fe- and Mn-oxides from a wide range of environments such as marine manganese nodules, soil nodules, and iron and manganese seeps (Ghiorse and Ehrlich, 1992).

### ORIGIN OF CAVE FMD

The oxide-rich layer was originally called “corrosion residue” and was believed to be the insoluble residue from either attack of corrosive air on the carbonate bedrock (Queen, 1994) or insoluble material remaining on the bedrock after sulfuric acid speleogenesis (Davis, 2000; Polyak and Provencio, 2001). In the process of condensation corrosion, warm moist air rises by way of Rayleigh-Bernard convection to a cave passage ceiling where water is condensed on the ceiling and upper walls, presumably because these areas are slightly cooler due to the geothermal gradient (Sarbu and Lascu, 1997). The condensed water absorbs CO<sub>2</sub> from the air to form carbonic acid that then corrodes the carbonate bedrock. Thus, in this model the FMDs represent the insoluble residue left after the dissolution of the bedrock by the weak acid. However, the Fe and Mn in the FMD is many times more enriched than can be explained by acidic dissolution of carbonate, either as a result

of condensation corrosion or from speleogenesis. Simple dissolution of Guadalupe carbonate bedrock by acids ultimately leaves a silica-rich residue with slightly enriched Fe<sub>2</sub>O<sub>3</sub> and barely detect-

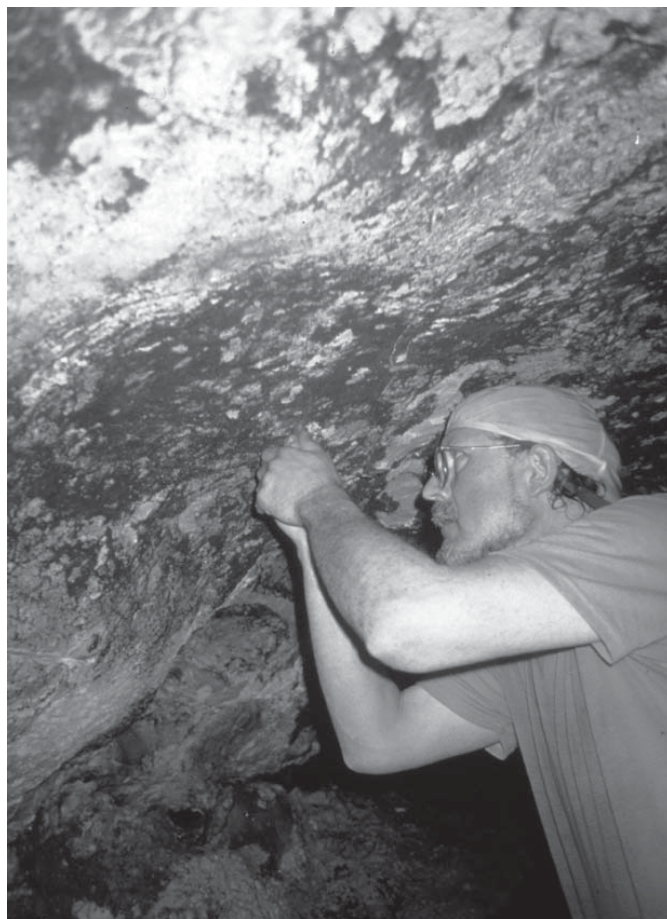


FIGURE 1. Collecting a sample of chocolate-brown ferromanganese from the ceiling of Snowing Passage in Lechuguilla Cave. Photo by Val Hildreth-Werker. See Plate 13B for a color image of a FMD.

able MnO, whereas the FMD are strongly enriched in Fe- and Mn oxides (Spilde et al., 2005).

Cunningham et al. (1994) observed evidence of microbial products in these deposits using scanning electron microscopy (SEM) and postulated that there may be a biotic process involved in the creation of the cave FMD (Cunningham et al., 1995). Northup et al. (2000, 2003), Boston et al. (2001), and Spilde et al. (2005) developed a model in which FMDs are the result of microbial activity. In this model, shown in Figure 2, microbes release organic acids, which break down the carbonate bedrock in the punk rock layer releasing Fe(II) and Mn(II) present in trace amounts in the carbonate minerals. Iron- and manganese-oxidizing microbes utilize the reduced Fe and Mn, oxidizing the elements as an energy source. The microbes may transport the released Fe and Mn from the punk rock zone with chelating ligands or through networks of exopolysaccharides. The oxidized respiration products build up in the oxide layer as Fe(III) and Mn(IV) oxides.

### CHEMISTRY AND MINERALOGY OF CAVE FMD

The cave FMDs are chemically and mineralogically distinct from the underlying bedrock, which consists of dolomite or calcite. In general, backreef bedrock is predominantly dolostone and the reef bedrock is predominantly calcite; detailed stratigraphy of the Guadalupe Mountains can be found in Hill (1996). Spider Cave is located entirely within the backreef, and Lechuguilla Cave spans both backreef and reef rocks. Table 1 lists the minerals that have been identified in the bedrock and FMD and their approximate abundances. Although calcite or dolomite are present in the FMD, their abundances are diminished, and new minerals, such as Al-hydroxides and Fe/Mn oxy-hydroxides have appeared. Lithiophorite  $[(\text{Al},\text{Li})\text{Mn}^{4+}\text{O}(\text{OH})_2]$ , nordstrandite and gibbsite  $[\text{Al}(\text{OH})_3]$ , goethite, kaolinite, and illite have been identified by XRD and SEM/EDX analysis. TEM examination revealed that much of the abundant Fe- and Mn-oxides are poorly crystalline, consisting of nanometer- and micrometer-sized domains of coherent crystal lattice. Todorokite  $[(\text{Mn}^{2+},\text{Ca},\text{Na},\text{Mg},\text{K})\text{Mn}^{4+}_3\text{O}_7 \cdot \text{H}_2\text{O}]$  and birnessite  $[(\text{Ca},\text{Na})_{0.5}(\text{Mn}^{4+},\text{Mn}^{3+})_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}]$  have been identified in the FMD by synchrotron micro-XRD (X-ray diffraction) (Boston et al., 2004).

Table 2 provides analyses of representative samples of the bedrock, punk rock and several colors of FMD to demonstrate the change in chemistry across the constituent layers. The major carbonate components, Ca and Mg, are depleted relative to original bedrock composition; the absolute concentration of most other elements is increased by the loss of carbonate. However, the relative proportion of the residual elements when compared to an insoluble element such as Ti varies significantly. Silica from clay and detrital quartz and feldspar in the bedrock is depleted relative to  $\text{TiO}_2$  in the dark FMD whereas Fe and Mn are generally much higher than expected. Iron and Mn in the oxide layer are hundreds to thousands of times enriched relative to the underlying bedrock;  $\text{Fe}_2\text{O}_3$  in the oxide layer may be as high as 78 wt% compared to less than 1 wt% in the bedrock and MnO as much as 22 wt% compared to 200 ppm or less in the bedrock. Not only are these elements strongly enriched, the Mn/Fe ratio increases by an order

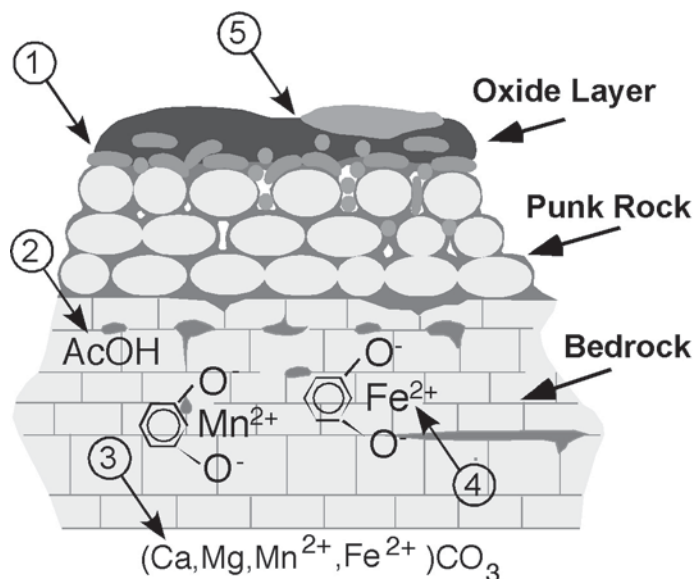


FIGURE 2. Schematic model of the ferromanganese deposit. Microbes (1) generate organic acids (2) that break down carbonate bedrock (3) releasing Fe(II) and Mn(II) from the carbonate mineral structure. The reduced elements are transported in the form of metal chelates (4) or exopolysaccharides to the microbial community where microbial oxidation takes place, with oxides accumulating at the cave-air interface (5). Modified from Northup et al., 2000.

of magnitude from around 0.07 in the bedrock and most of lighter colored FMDs to 0.8 in the dark FMD, suggesting an enrichment of manganese over iron (Spilde et al., 2005). Likewise, the porosity increases and bulk density decreases dramatically from bedrock, through punk rock, to the oxide layer, which is usually much less than  $1 \text{ g/cm}^3$  after drying. The strong enrichment of Fe and Mn oxides in the FMD and the marked increase of Mn:Fe ratios indicate a mass transfer from the punk rock to the outer oxide layer, while Ca and Mg are removed from both layers and Si is depleted in the outer layer.

### MICROBIOLOGY OF CAVE FMD

Northup et al. (2000, 2003) demonstrated that there is a diverse microbial community present in the FMD in Lechuguilla and Spider Caves, including a high percentage of mesophilic Archaea in one site. Identified from community DNA were clones whose closest relatives are iron or manganese oxidizers or reducers, although, in general, the similarity values were low. Nearest relatives known to oxidize or reduce iron or manganese include *Hyphomicrobium*, *Pedomicrobium*, *Leptospirillum*, *Stenotrophomonas*, and *Pantoea* (Northup et al., 2003). DNA extracted from cultures inoculated with FMD from the Rainbow Room in Lechuguilla Cave more clearly demonstrated the presence of putative manganese oxidizers with closest relatives including species of *Bacillus* and *Alcaligenes*, organisms that have been reported to oxidize manganese (e.g., Francis and Tebo, 2002 for *Bacillus* and Abdrashitova et al., 1990 for *Alcaligenes*).

Epifluorescent microscopy showed extensive microbial communities present in both the oxide layer and punk rock (on the

TABLE 1. Minerals identified in the bedrock and ferromanganese, with approximate abundance.

Mineral	Formula	Approximate abundance:	
		omanganese	Bedrock
Mn-oxides:			
Birnessite	(Ca,Na) <sub>0.5</sub> (Mn <sup>4+</sup> ,Mn <sup>3+</sup> ) <sub>2</sub> O <sub>4</sub> •1.5H <sub>2</sub> O	m	-
Lithiophorite	(Al,Li)MnO <sub>3</sub> (OH) <sub>2</sub>	M	-
Rancieite	(Ca, Mn <sup>2+</sup> )Mn <sup>4+</sup> O <sub>9</sub> •3(H <sub>2</sub> O)	T	-
Todorokite	(Mn <sup>2+</sup> ,Ca,Na,Mg,K)Mn <sub>3</sub> O <sub>7</sub> •H <sub>2</sub> O	m	-
Fe-oxides:			
Goethite	α-FeO(OH)	M	-
Hematite	Fe <sub>2</sub> O <sub>3</sub>	m	T
Lepidocrocite	FeO(OH)	m	-
Clays:			
Dickite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	T	T
Halloysite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	T	-
Illite	(K,H <sub>3</sub> O)(Al,Mg,Fe) <sub>2</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> [(OH) <sub>2</sub> , (H <sub>2</sub> O)]	M	T
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	m	T
Montmorillonite	(Na,Ca) <sub>0.3</sub> (Al,Mg) <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> •n(H <sub>2</sub> O)	-	T
Al-hydroxides			
Diaspore	α-AlO(OH)	T	-
Gibbsite	Al(OH) <sub>3</sub>	m	-
Nordstrandite	Al(OH) <sub>3</sub>	M	-
Phosphates:			
Apatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH,F,Cl)	T	T
Goyazite	SrAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> •(H <sub>2</sub> O)	m	-
Monazite	(Ce,La)PO <sub>4</sub>	-	T
Rhabdophane	(Nd,Ce,La)PO <sub>4</sub> •H <sub>2</sub> O	T	-
Svanbergite	SrAl <sub>3</sub> (PO <sub>4</sub> )(SO <sub>4</sub> )(OH) <sub>6</sub>	m	-
Others:			
Calcite	CaCO <sub>3</sub>	m	M
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	m	M
Ilmenite	FeTiO <sub>3</sub>	T	T
Rutile	TiO <sub>2</sub>	T	T
Quartz	SiO <sub>2</sub>	m	m

M = major (&gt; 10%)

m = minor (&lt; 10%)

T = trace (&lt; 1%)

order of 10<sup>7</sup> cells per cm<sup>3</sup>). Analysis of total cell numbers showed that highest numbers of cells were seen at interfaces, the pink/white interface between oxide layer and punk rock, and the black/brown interface between the oxide layer and the atmosphere of the cave. Studies done to ascertain the portion of metabolically active cells present demonstrated that higher activities are seen in darker FMDs and in the punk rock, where higher numbers of prosthecate (i.e., stalked) bacteria are observed. We believe that this lends support to a biogenic hypothesis for FMDs because two known manganese oxidizers (*Pedomicrobium* and *Hyphomicrobium*) are prosthecate bacteria that are similar in morphology to those observed in FMDs and punk rock. Organisms cultured from the cave deposits have slowly produced in the laboratory an array of Fe- and Mn oxideminerals that are present in the cave FMDs, e.g., birnessite (Boston et al., 2001).

### SPELEOSOL: A NEW TYPE OF SUBTERRANEAN SOIL

Cave FMD are similar in many ways to laterite soils (oxisols). Sedimentary 2:1 clays (e.g., smectite, illite) are converted to 1:1 clays (e.g., kaolinite) (Sposito,1989); soluble elements such as K, Ca, Na, Mg, Si are leached from the system; other elements such as Al, Fe and Mn are enriched in sesquioxides; and insoluble trace elements (Ti, Zr, Nb) are enriched (Buol and Eswaran, 2000). Other trace elements like Ni are sequestered in oxides, especially Mn-oxides that are powerful scavengers of transition metals (Manceau et al., 2002).

Both todorokite and birnessite have been identified in these deposits. These minerals are also present in both soils and desert varnish, environments believed to be strongly influenced by microbial communities. Birnessite is the most common Mn-mineral found in soils (Sposito,1989) and todorokite is widely cited

as a product of microbial Mn(II) oxidation (Tebo et al., 1997 and references therein). Desert varnish, partially a product of microbial activity (Nagy et al., 1991), contains clays interlayered with Mn- and Fe-oxide minerals. Like desert varnish, a diverse microbial community has been identified in the cave deposits by 16S rDNA sequence analysis, and includes microorganisms whose closest relatives are manganese- and iron-oxidizing bacteria and nitrogen-fixing bacteria. Both communities have yielded genetic sequences that group with species from the *Actinobacteria*, *Pantoea agglomerans*, *Comamonas* spp., *Rhizobium* spp., and *Bacillus* spp.

The similarities in mineral composition to that of some soils and the presence of a diverse microbial community suggests that these cave deposits may undergo a development process similar to terrestrial soil. Both chemical and microbial processes may influence the formation of the ferromanganese cave deposits. Chemical weathering from the condensation of weak carbonic acid in Bernard-Rayleigh convection cells in the caves may contribute to the breakdown of the bedrock carbonate (Queen 1994). However, microbial breakdown of bedrock probably plays a more significant role. The oxidation of Fe(II) and Mn(II) releases H<sup>+</sup> ions, and the microorganisms themselves may release organic acids, both of which contribute to dissolution of carbonate. The residual weathered products, rich in secondary minerals and organic matter, are essentially subterranean soils. Thus, the term "corrosion residue" to describe these deposits is misleading, since it suggests that the material is derived only from condensate corrosion or acid speleogenesis. On the other hand, ferromanganese deposits is a general term that refers to composition only and does not suggest an origin. Perhaps a more appropriate term for these deposits, referring to their soil-like properties and derivation, would be "*speleosol*" or cave soil.

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TABLE 2. Chemical analyses of representative samples of bedrock, punk rock and several different colored oxide layers.

	Bedrock dolostone	Punk rock	Pink	Red	Dark brown	Black
% Lost in						
Drying <sup>a</sup>	n.a.	6.6	14.2	17.5	59.2	60.8
SiO <sub>2</sub>	1.57	2.74	5.00	14.30	3.05	0.45
Al <sub>2</sub> O <sub>3</sub>	0.38	1.76	3.03	10.15	2.48	16.12
Fe <sub>2</sub> O <sub>3</sub> <sup>b</sup>	0.1	0.86	0.59	2.87	78.80	17.19
MnO	<0.01	0.06	0.03	0.14	0.45	21.64
MgO	21.03	20.6	20.30	1.95	1.07	1.30
CaO	30.57	25.9	28.20	32.20	0.49	8.40
Na <sub>2</sub> O	<0.01	<0.01	<0.01	<0.01	0.09	0.08
K <sub>2</sub> O	0.09	0.34	0.66	1.57	0.03	0.04
TiO <sub>2</sub>	0.03	0.13	0.18	0.64	0.30	1.05
P <sub>2</sub> O <sub>5</sub>	0.01	0.03	0.05	0.11	0.88	3.72
% Lost on						
Ignition	45.89	45.09	41.05	32.62	14.68	21.49
Density (g/cm <sup>3</sup> )	2.71	1.14	0.29	0.55	0.14	0.11
%N (whole rock)	BDL	0.03	BDL	n.a.	0.05	BDL
%C (whole rock)	12.4	12.5	11.43	n.a.	0.02	1.10
%N (organic) <sup>c</sup>	0.033	0.017	0.026	0.022	0.016	BDL
%C (organic)	0.795	8.839	7.277	0.016	0.043	0.085

Notes: n.a., not analyzed; BDL, below detection limit.

<sup>a</sup>Weight lost on drying; chemical analyses reported on dry weight basis.

<sup>b</sup>Total Fe reported as Fe<sub>2</sub>O<sub>3</sub>.

<sup>c</sup>Determined after acid digestion of whole rock.

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