

THE MINERALOGY AND TRACE ELEMENT CHEMISTRY OF BLACK MANGANESE OXIDE DEPOSITS FROM CAVES

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Abstract: Free surface streams in caves and their surface infeeders often contain pebbles and cobbles coated with black manganese oxide minerals. Coating thicknesses vary from fractions of a millimeter to a few millimeters. In addition, a few caves contain loose masses of black oxide material. The results reported here are based on examination of 39 specimens and detailed chemical analyses of 18 of them. Most of the coatings are amorphous to x-rays, with at best, only a few broad diffraction lines. Infrared spectroscopy shows that most of the specimens are birnessite, with evidence for romanechite, ranceite, and pyrolusite in a few specimens. All specimens contain both iron and manganese, but the Mn/Fe ratio varies widely. Many specimens are enriched in Ba but depleted in Sr. The manganese and iron oxides contain the transition metals Co, Cu, Ni, V, and Zn in concentrations greater than 0.5 wt% in some specimens. Minor Cr and Mo also occur. Given the extremely low concentrations of these elements expected in freshwater streams in carbonate terrains, the manganese oxides exert a dramatic amplifying effect over the expected background. Manganese oxides appear to act as a dosimeter for heavy metals in karst waters.

INTRODUCTION

Stream cobbles, chert ledges, and other silica substrates exposed to free surface streams in limestone caves are frequently coated with a black substance usually labeled manganese oxide. In most localities, the coatings vary in thickness from fractions of a millimeter to a few millimeters. A few caves are known in which more massive black coatings or loose deposits many centimeters thick occur. As a caveat, it is not appropriate to label every black deposit seen in caves as manganese oxide. As noted by Hill (1982), soot from early explorer's torches, carbonized organic matter, and other black materials may occur. However, most black stream-bed coatings examined in this study have been identified as manganese oxide, and these coatings are the subject of the present paper.

The oxides of Mn³⁺ and Mn⁴⁺ display a very complex mineralogy, with many crystal structures and many variations in trace element chemistry (Post, 1999). Manganese oxide minerals are widely known from stream sediments, from soils, and from deep-sea nodules. Synthetic manganese oxides are important in technology, particularly as battery materials. It is generally agreed that the oxidation of the soluble Mn²⁺ to trivalent or tetravalent manganese in near surface environments is mediated by microorganisms. There is a very large body of earlier literature that has been reviewed by Tebo et al. (1997) and includes some quite recent work (Jürgensen et al., 2004).

For the most part, the manganese oxides that occur in caves are very poorly crystallized, thus making the identification of the mineral phase difficult. Birnessite has been identified as the most commonly occurring mineral (Moore, 1981; Kashima, 1983). Other manganese minerals

that have been reported from caves, with identifications of varying degrees of confidence, include chalcophanite, cryptomelane, hausmannite, pyrolusite, ranceite, romanechite, and todorokite (Hill and Forti, 1997). Manganese oxides also occur in karst solution cavities (Jones, 1992). Manganese oxide deposits are listed among cave minerals of predominantly microbial origin (Northup and Lavoie, 2001; Spilde et al., 2005). Evidence for specific microorganisms has been provided by Peck (1986) and by Northup et al. (2003).

The present paper is concerned with manganese oxides as scavengers for transition (iron-group) metals in karst environments. Ore-quality concentrations of transition group metals are, of course, well known from marine manganese oxides (Burns and Burns, 1978). Deposition of metal-containing manganese oxides in a surface stream has been measured (Carpenter and Hayes, 1980). Cave deposits form in a fresh-water environment with relatively few sources for transition group metals. However, the few reported analyses (Moore, 1981; Peck, 1986; White et al., 1985) reveal metals such as zinc and nickel at the fractional percent level. Onac et al. (1997) reported high concentrations of rare earth elements in the manganese oxides in a cave in Romania. The present paper reports a more systematic investigation that reveals high concentrations of transition group elements in a variety of cave manganese deposits in the eastern and central United States.

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Table 1. Sources of specimens used for manganese oxide characterization.

Sample No.	Cave Name	Location	Sample Description
208	Weber Cave	Iowa	Loose black powder
209	Muenster Cave	Iowa	Loose black powder
214	Wind Cave	South Dakota	Brown earthy mass
271	Wind Cave	South Dakota	Brown dirt from geode
531	Mammoth Cave	Kentucky	Black coating on chert ledge
555	Parker Cave	Kentucky	Large pebbles with flaky brown coating
575	Jewel Cave	South Dakota	Thick massive black deposit in cave passage
580	Devil's Icebox	Missouri	Thick black coatings from stream passage
619	Mammoth Cave	Kentucky	2 mm coating on chert ledge
622	Snail Shell Cave	Tennessee	1 mm dull black coating on flowstone
627	Cumberland Caverns	Tennessee	Loose brown-black sooty material on chert
632	Tumbling Rock Cave	Alabama	0.2–0.5 mm coating on pebble
636	Priddy Cave	Kentucky	Thick coating on limestone chip in stream bed
639	Colossal Cave	Kentucky	Thin coating on chert
646	Anvil Cave	Kentucky	Black coating on sandstone pebble
650	Matt's Black Cave	West Virginia	3–5 mm massive black crust
82MM003	Jewel Cave	South Dakota	Loose black powder
96MM001	Hineman Cave	Pennsylvania	Soft black flowstone with orange bands

EXPERIMENTAL METHODS

SAMPLE DESCRIPTIONS

A total of 39 specimens of black coatings and deposits were collected from caves, mostly in the eastern United States. Many of these were stream cobbles, either from active streams or from abandoned high-level cave passages. Many of the coatings were thin, fractions of a millimeter, so that it was not possible to physically remove sufficient sample for analysis. About half, 18 specimens, were either bulk deposits or were coatings of sufficient thickness that they could be sampled for analysis (Table 1). The samples are identified by their number in a master collection of cave material maintained by the senior author.

For those specimens of sufficient mass, milligram quantities of the oxide coatings were scraped off, care being taken to avoid contamination by the substrate and by sample handling. The manganese oxide coatings were soft enough to be easily removed. Bulk deposits could be sampled directly. Solid chips were ground in an agate mortar so that all initial samples were powders.

CHARACTERIZATION METHODS

Textures and rough bulk compositions of the black coatings were measured using a scanning electron microscope equipped with an energy-dispersive X-ray detector (EDX). The EDX spectra confirmed that the coatings were indeed oxides of manganese and also revealed major elements such as Ca, Ba, Al, and Si.

X-ray diffraction was of limited value for phase identification because of the very small particle size and structural disorder within the samples. Infrared spectroscopy was more useful because it allowed comparison of the

spectra of the cave deposits with the reference spectra established by Potter and Rossman (1979). All spectra were measured by the KBr pellet technique. One mg of sample was ground with 200 mg of KBr and vacuum cold-pressed into a compact disk that was then inserted into the spectrometer. Several older spectra were obtained from a Perkin-Elmer model 283 dispersive spectrometer. More recent spectra were obtained with a Nicolet Fourier transform spectrometer.

Samples for chemical analysis were dissolved in hydrochloric acid, and the resulting solutions analyzed for cations by DC plasma emission spectroscopy. The limit of detection for the method was 3 ppm with respect to the original solid sample.

RESULTS

CHEMICAL CHARACTERIZATION

Chemical analyses of the deposits are displayed for the powders and bulk specimens in Table 2 and for the coatings in Table 3. The analyses are reported as weight percent oxide with respect to the original solid sample. The total masses of the various component oxides do not add up to 100%, and some samples fall far short of 100%. There are three sources for this discrepancy. Most of the analyses were conducted on a few milligrams of material scraped from chert layers or sandstone stream cobbles. The scrapings were weighed and then dissolved in HCl. Excess silica would be included in the original weighing but not in the final solution injected into the DC plasma. This was confirmed by re-analyzing two of the bulk specimens (for which there was adequate sample) by a fusion technique that took the entire sample into solution. Sample 214

Table 2. Chemical analyses of massive and loose powder deposits. All compositions in wt%.

Oxide	Sample Number							
	82MM003	209	575	627	208	96MM001	214	271
Al ₂ O ₃	0.23	0.11	0.63	11.3	0.21	1.89	0.71	0.39
B ₂ O ₃	0.054	0.046	0.013	0.029	0.031	0.081	0.023	0.025
BaO	7.73	1.84	8.83	0.3	5.13	0.18	0.96	0.31
CaO	8.17	7.69	2.52	1.63	5.11	3.67	4.68	4.71
CoO	0.26	0.22	0.3	0.36	0.21	0.11	0.003	0.005
Cr ₂ O ₃	0.038	0.039	0.007	0.13	0.009	0.01	0.021	0.01
CuO	0.51	0.045	0.17	0.044	0.04	0.056	0.083	0.018
Fe ₂ O ₃	0.68	0.95	3.29	33	0.82	21.5	9.53	3.06
K ₂ O	0.65	0.13	0.36	0.085	0.37	0.082	0.16	0.15
MgO	2.11	2.39	1.15	3.13	2.4	1.08	0.69	0.21
MnO ₂	67.39	64.94	58.82	13.72	53.92	24.63	8.47	4.17
MoO ₃	0.052	0.044	0.05	0.12	0.051	0.036	0.038	0.035
Na ₂ O	0.46	0.24	0.29	0.88	0.69	0.28	0.072	0.098
NiO	0.66	0.37	0.43	0.28	0.76	0.49	0.13	0.069
SiO ₂	0.33	0.36	0.24	1.38	0.33	1.66	0.66	0.61
SrO	0.2	0.006	0.18	0.15	0.049	0.011	0.03	0.003
TiO ₂	0.006	0.015	0.052	0.34	0.015	0.003	0.047	0.006
V ₂ O ₅	0.72	0.014	0.94	0.28	0.014	0.025	0.092	0.034
ZnO	0.14	1.87	0.091	0.39	1.37	0.068	0.072	0.023
ZrO ₂	0.1	<0.003	<0.003	0.19	<0.003	<0.003	<0.003	<0.003
Total	90.49	81.32	78.36	67.74	71.53	55.87	26.47	13.78

Table 3. Chemical analyses of coatings. All concentrations in wt%.

Oxide	Sample Number									
	531	580	555	650	619	622	636	646	632	639
Al ₂ O ₃	6.62	2.47	5.76	3.8	7.56	4.68	2.77	7.44	9.97	1.54
B ₂ O ₃	0.014	<0.003	0.017	0.026	0.071	0.035	0.019	0.023	0.048	0.032
BaO	0.64	0.278	0.72	0.77	0.44	0.45	1.62	0.26	0.24	0.31
CaO	20.5	5.71	4.09	4.76	4.34	5.82	10.7	2.06	3.26	1.96
CoO	0.074	0.06	0.08	0.13	0.036	0.065	0.18	0.57	0.18	0.11
Cr ₂ O ₃	0.038	<0.003	0.006	0.067	0.047	0.046	0.1	0.081	0.062	0.067
CuO	0.56	0.029	0.024	<0.003	<0.003	<0.003	0.004	0.013	<0.003	0.011
Fe ₂ O ₃	4.09	3.25	5.86	3.19	6.58	4.23	2.59	2.48	4.67	1.72
K ₂ O	0.13	0.39	0.14	0.21	0.12	0.27	0.31	0.06	0.049	0.078
MgO	1.37	0.7	0.96	0.79	0.93	0.64	0.86	0.47	0.44	0.47
MnO ₂	20.46	45.34	31.49	34.06	20.22	25.12	20.95	20.95	17.65	8.99
MoO ₃	0.052	0.036	0.044	0.081	0.03	0.031	0.12	0.1	0.074	0.078
Na ₂ O	0.099	0.3	0.082	0.15	0.13	0.12	0.24	0.16	0.12	0.13
NiO	0.98	0.094	0.22	0.15	0.15	0.038	0.13	1.3	0.62	0.11
SiO ₂	1.67	0.14	0.75	0.47	1.26	0.54	0.16	0.13	0.38	0.27
SrO	0.072	0.027	0.047	0.048	0.067	0.031	0.057	0.029	0.047	0.026
TiO ₂	0.072	0.011	0.055	0.076	0.078	0.041	0.11	0.091	0.1	0.088
V ₂ O ₅	0.037	0.067	0.035	0.15	0.071	0.072	0.24	0.21	0.14	0.17
ZnO	0.17	1.56	0.33	0.077	0.18	0.021	0.085	1.58	0.18	0.056
ZrO ₂	0.17	<0.003	<0.003	0.041	<0.003	0.026	0.22	0.081	0.053	0.066
Total	57.82	60.47	50.71	49.05	42.31	42.27	40.46	37.73	33.28	16.29

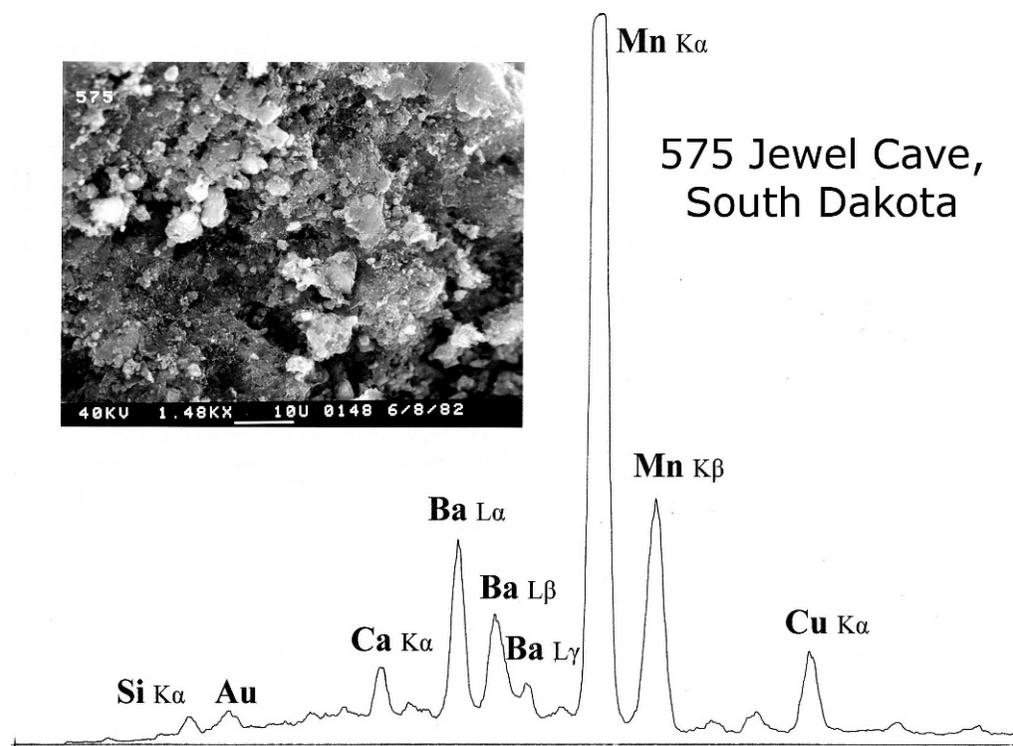


Figure 1. SEM image and EDX spectrum of specimen 575 from Jewel Cave, South Dakota. Note that this sample is exceptionally barium-rich. The EDX spectrum is a plot of X-ray intensity versus X-ray energy. Characteristic lines for various elements are labeled.

contained 41.0 wt% SiO₂, compared with 0.66% in the acid solution. Sample 580 contained 12.3% SiO₂ by fusion, compared with 0.14% in the acid solution. The second source of discrepancy is that most of the samples are hydrated to some extent, but the results were calculated only as the oxides and did not account for either OH⁻ or bound water. The third, and minor, source is that a few samples contain some carbonate that is taken into solution along with the manganese oxide, but the CO₂ component does not appear in the analysis, although Ca does. Tables 2 and 3 contain the original analytical data. Further interpretation was based on elemental concentrations that were normalized to the sum of oxide components given at the bottoms of the tables.

Thermogravimetric analysis was conducted on four of the samples (214, 575, 580, and 650) from ambient to 1000 °C. There was a continuous mass loss of 15–20% up to 700 °C, above which the weight remained constant. 5–10% of the mass loss occurred below 150 °C and likely represents water and easily decomposed hydrates.

STRUCTURAL CHARACTERIZATION

SEM images of two samples are superimposed on their X-ray emission spectra (Figs. 1 and 2). The Jewel Cave sample (575) is a thick, massive deposit that occupies the floor of one small passage to a depth of at least tens of centimeters. The laboratory sample was several centimeters

thick and free of extraneous contamination. The SEM image reveals little structure at the micrometer scale. This locality had been previously examined by Moore (1981), who identified the mineral as hollandite, a conclusion consistent with the high Ba concentration shown in the EDX spectrum. The Mammoth Cave sample (531) was taken from a several-millimeters-thick layer that had been deposited on a chert ledge just above the floodwater zone. The SEM image reveals a granular structure with individual particles about 3–5 μm in diameter. The appearance of Al and Si in the EDX spectrum suggests contamination by silica and silicate minerals in the coating itself; not all contamination is due to the substrate. SEM images of two additional samples, both loose powders from cave floors, (Fig. 3) show a filamentary structure that may indicate a microbial origin. Well-crystallized manganese oxides do occasionally appear in caves, for example, romanèchite from Corkscrew Cave, AZ, which gives a sharp X-ray powder pattern (Onac et al., 2007).

Infrared spectra of two bulk samples display the expected features of manganese oxides (Fig. 4). The Muenster Cave, IA sample (209) was a loose powder; the Jewel Cave sample was a massive, consolidated chunk. The broad bands at 3280 and 3400 cm^{-1} are the stretching modes of OH groups. The band at 1610 is the H₂O bending mode, which shows that at least some of the OH is H₂O. The intense band at 465 and the group of bands centered at

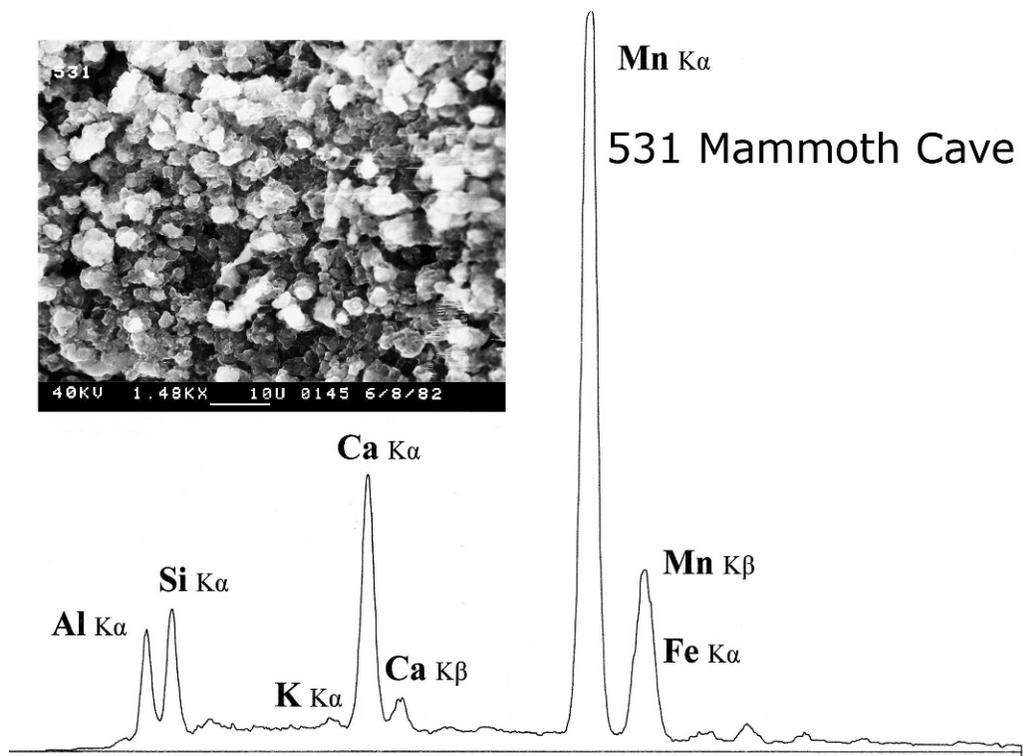


Figure 2. SEM image and EDX spectrum of specimen 531 from Mammoth Cave, Kentucky.

525 cm^{-1} are the stretching modes of the MnO_6 octahedra that are the fundamental building blocks of the manganese oxide mineral structures.

Infrared spectra also reveal the presence of mineral contaminants (Fig. 5). Specimen 214 contains a great deal of silica, which appears in the IR spectrum as the intense band at 1030 cm^{-1} . The weaker bands at 795, 772, and 690 cm^{-1} identify the contaminant mineral as quartz.

Specimen 531 contains both silica and carbonate, the latter producing the strong absorption at 1425 cm^{-1} .

Examination of the Mn-O stretching mode on the four samples in Figures 4 and 5 and three additional spectra (only the Mn-O band) in Figure 6 makes clear that the manganese mineral coatings deposited in cave environments have distinctly different structures. The cave samples, as cold water deposits, are crystallized only at

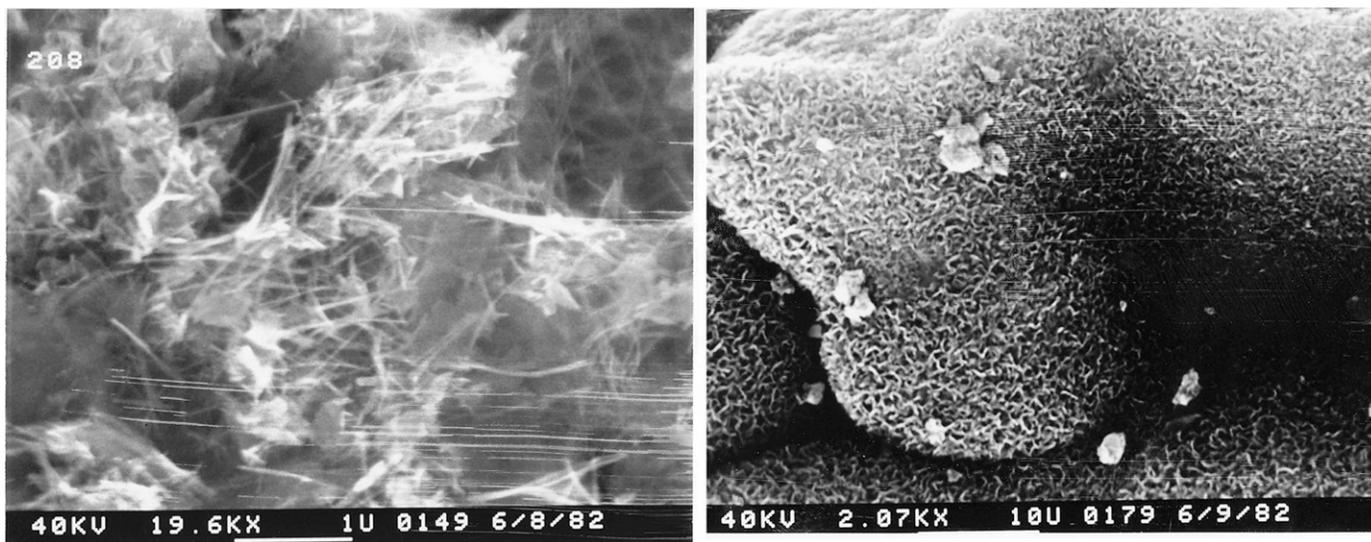


Figure 3. SEM images. Left: sample 208, Weber Cave, Iowa, showing filamentary structure. Right: sample 209, Muenster Cave, Iowa, showing crenulated surface structure.

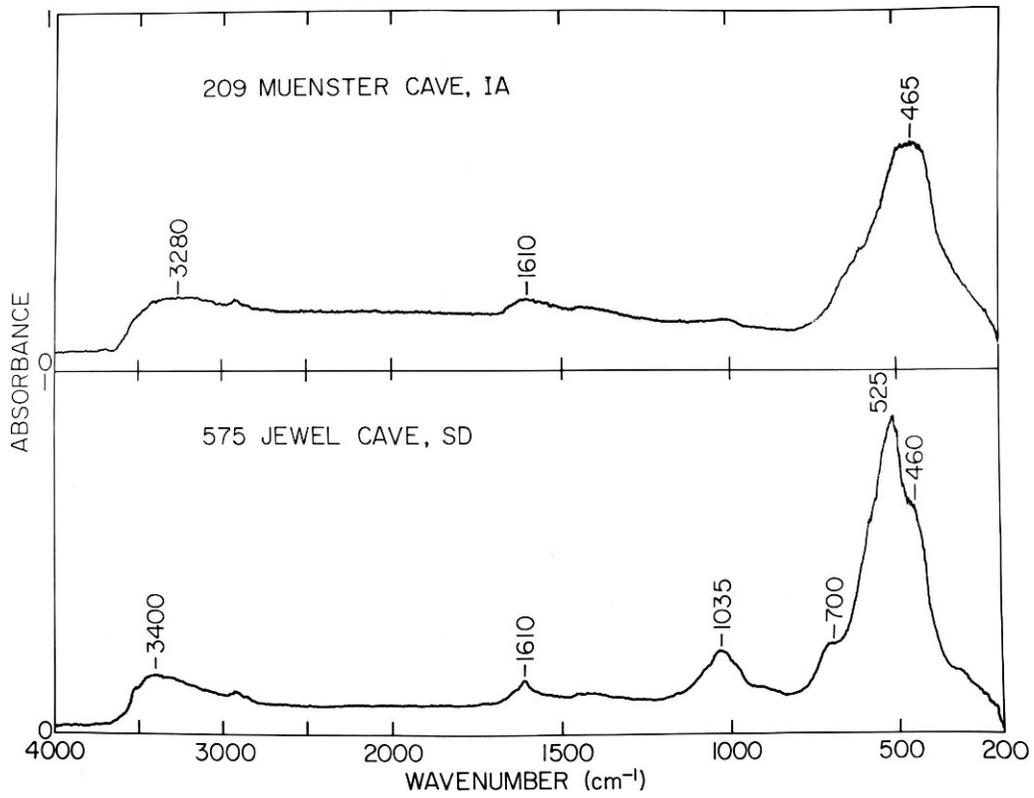


Figure 4. Infrared spectra of two phase-pure manganese oxides.

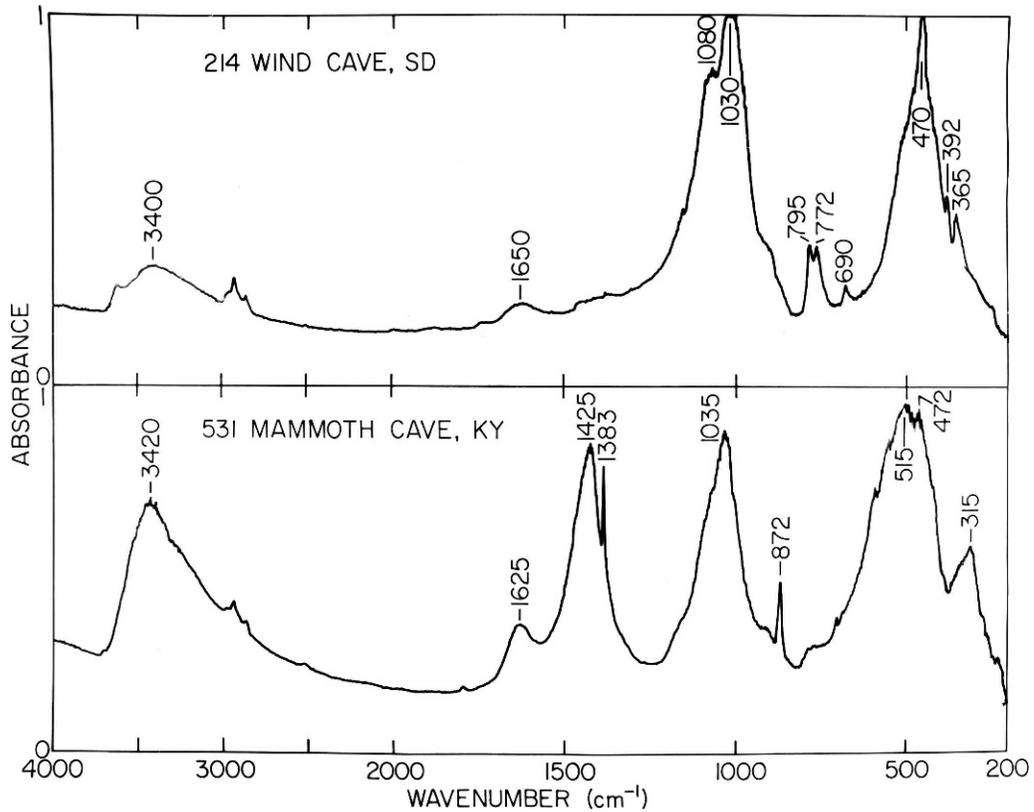


Figure 5. Infrared spectra of two contaminated manganese oxides.

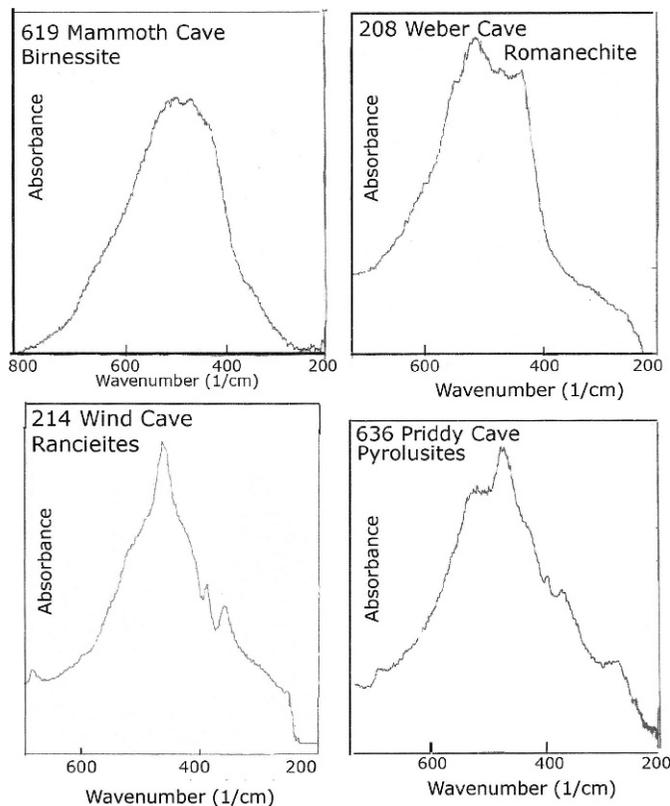


Figure 6. Infrared spectra of the Mn-O stretching region of four manganese oxides.

the nano-scale so that their X-ray diffraction patterns are essentially featureless. Tentative interpretation of the IR spectra of 14 of the 18 samples gives mineral identifications of eight birnessites, one romanechite, two rancieites, and three pyrolusites.

HEAVY METAL CHEMISTRY IN CAVE MANGANESE OXIDE MINERALS

IRON/MANGANESE RELATIONS

There is a rough correlation between iron and manganese in the deposits (Fig. 7). All of the Mn-rich deposits and coatings contain at least some Fe. There appears to be a gap between Fe-rich Mn deposits and three samples that might be called Mn-containing iron deposits.

ALKALINE EARTH RELATIONS

Normalized concentrations of BaO, SrO, CaO, and MgO are displayed in Figure 8. The high Ca concentration is expected, since Ca is a component of many of the manganese oxide minerals and the deposits examined all formed from carbonate waters. Many of the samples are Ba-rich, with BaO concentrations between 1 and 10 wt%. What is surprising is that Sr seems to be strongly suppressed. Concentrations of SrO range from less than 0.01 wt% to, at most, a few tenths of a percent, almost two

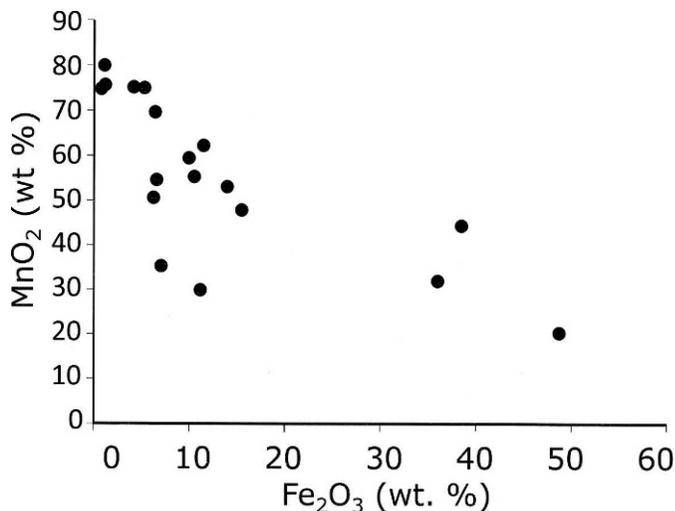


Figure 7. Plot of iron versus manganese content. Iron is calculated as Fe₂O₃ and manganese as MnO₂. Both are expressed as a percentage of the final sum of analyzed constituents.

orders of magnitude less than BaO. Carbonate mineral deposits in caves (speleothems), usually composed of calcite or aragonite, contain more Sr than Ba.

TRANSITION METAL RELATIONS

Cave Mn deposits, like ocean floor nodules and other stream Mn deposits, contain substantial quantities of transition metals (Fig. 9). Of the seven trace metals plotted in Figure 9, CoO, NiO, V₂O₅, and ZnO are present in some samples at concentrations greater than one wt%. The samples represent a range of localities, mostly in the eastern United States. The cave streams from which the samples were taken are mostly in the headwaters of their associated drainage basins. Background concentrations of transition metals in the streams are not known for any of the localities and, indeed, the streams are no longer present in many of the cave passages.

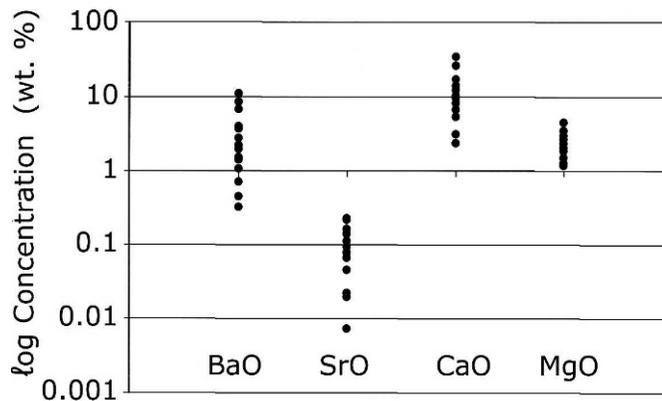


Figure 8. Distribution of alkaline earth elements calculated as the oxides.

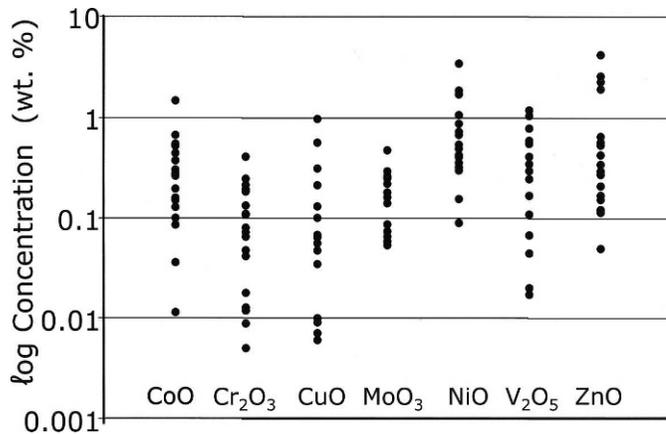


Figure 9. Distribution of the transition elements Co, Cr, Cu, Mo, Ni, V, and Zn.

Analyses of transition metals in freshwater surface streams are rare, and the few observed concentrations are highly variable. Such sparse data as are available suggest that transition metal concentrations would be expected to be in the range of a few parts per billion. At the high end are elements such as V and Zn in the range of tens of parts per billion. At the low end, is Co at fractions of a parts per billion. Yet Co appears in the Mn-deposits at concentrations from 0.01 to 1 wt% (10^5 to 10^7 ppb). The Mn-oxide minerals in general, and birnessite (δ -MnO₂) in particular, are extremely effective adsorbers of transition metals. The enhancement factors between the background concentration in the cave streams or groundwater and the concentration in the deposits are on the order of 10^6 . There is the possibility that the concentrations of transition metals in manganese oxides reflect the concentrations in the surface environment. If this should prove to be the case, the manganese oxides would act as a dosimeter for other metals in the environment.

CONCLUSIONS

Black coatings on stream cobbles and on chert ledges commonly found in limestone caves were shown to consist of very poorly crystalline manganese oxides. Mineral identification by infrared spectroscopy suggests birnessite to be the most common phase. Complete chemical analyses were obtained for 18 specimens. Among the alkaline earth elements, the concentration of Ba is enhanced, while the concentration of Sr is suppressed. The transition metals Co, Cr, Cu, Mo, Ni, V, and Zn were found in most of the manganese deposits at concentrations in the fractional percent to percent range. Manganese oxides are deposited in caves from freshwater streams that often sink into the cave system from headwaters on nearby non-carbonate rocks. Comparison of the concentrations of transition metals found in the deposits with expected concentrations in the source streams suggests an enhancement factor on the order of 10^6 .

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