

Mineralogy of manganese dendrites and coatings

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Abstract

Infrared spectroscopic study of desert varnish, manganese dendrites, river deposits, and other manganese oxide concentrations of the terrestrial weathering environment has shown that the morphological distinctions among them have a sound basis in differences in their mineralogy. The manganese oxide in manganese dendrites collected in surface exposures is either romanechite or a hollandite-group mineral. These are mixed with varying amounts of silicate minerals, which are a passive substrate for the oxide deposition. Dendrites collected in underground mine workings are todorokite. Manganese stream deposits are generally birnessite with minor amounts of silicate minerals; one nsutite stream deposit has been identified. Crack deposit mineralogy resembles that of manganese dendrites. Cave and subglacial deposit mineralogy resembles that of manganese stream deposits. Although dendrites have long been considered to be pyrolusite, no example of pyrolusite mineralogy has been identified.

Introduction

Manganese oxide concentrations are a common product of terrestrial weathering processes. Concentrations with variable morphology, chemistry, and physical properties occur in diverse environments throughout the world: desert varnish in arid and semi-arid regions, manganese dendrites within and on the surfaces of rocks, deposits within cracks in rocks, and associated with rivers, caves, and glaciers.

Determination of manganese oxide mineralogy of these materials by X-ray diffraction has been difficult or impossible owing to the finely particulate and disordered nature of the manganese oxides and the presence of silicate phases as major components of the deposits. For this reason the structural and genetic relations among them are poorly understood.

Infrared spectroscopy is particularly useful for mineralogical analyses of manganese oxide concentrations. It eliminates ambiguity frequently caused by silicate components (such as the confusion of kaolinite and birnessite). Because it is sensitive to short-

range order, it provides mineralogical information on even the most disordered and finely-particulate phases. Its successful application to determination of desert varnish mineralogy (Potter and Rossman, 1979a) led us to systematically investigate its usefulness for determinative mineralogy of the manganese oxides (Potter and Rossman, 1979c).

This paper presents the results of a mineralogical study of a wide range of manganese oxide concentrations of the terrestrial weathering environment. Infrared spectroscopy indicates distinct differences in mineralogy which can be correlated with the morphology of the deposit and its depositional environment.

Experimental

We prepared powdered samples as follows: milligram quantities of the manganese oxide concentrations were removed from their substrates by scraping with a tungsten needle under 20× magnification. The resultant material was examined under 40×, light-colored contaminants removed, and the material ground under toluene to a fine powder in a boron carbide mortar and pestle. When carbonate was present in the sample, it was removed by treatment with 1.0 M acetic acid for 5 minutes prior to any further analysis. Manganese and iron oxides were extracted

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from the samples by the sodium dithionite procedure (Mehra and Jackson, 1960), which was shortened to a single 5-minute extraction to minimize the effect on the silicates. Infrared spectra of the samples and their dithionite-extracted residues were obtained with a Perkin-Elmer Model 180 spectrophotometer on 0.50 mg of powdered sample dispersed in 200 mg KBr and dried overnight at 120°C under vacuum to remove water adsorbed on the KBr. This treatment affected only those infrared features due to adsorbed water. In the figures we have presented spectra at various percentages of their true intensities to facilitate comparison. The intensity for any sample may vary by a factor of 2 or 3 due to differences in its particle size and degree of dispersion in the KBr. We obtained infrared spectra of the manganese oxides in samples by computer generation of difference spectra (for example, Fig. 1). Absorption due to silicates was removed from a spectrum (Fig. 1C) by subtracting from it that fraction of the extracted residue spectrum necessary to null the absorption near 1000 cm^{-1} (Fig. 1D), which is due wholly to silicates. The result-

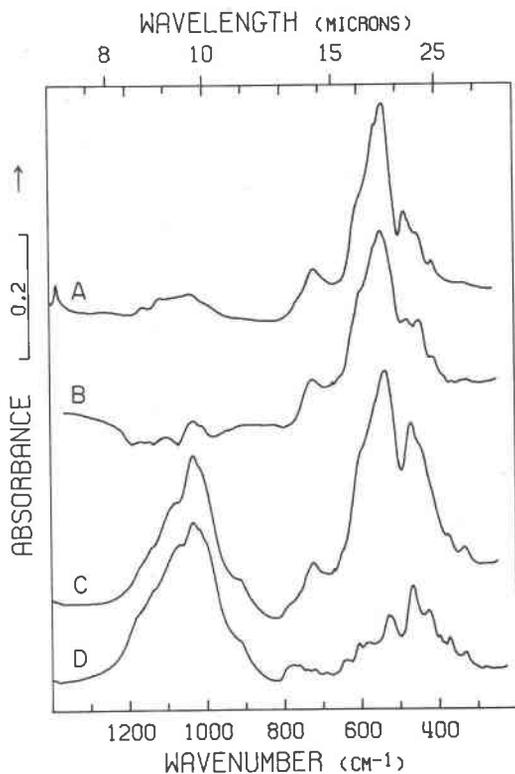


Fig. 1. Infrared spectra identifying romanechite in manganese dendrite No. 17: (A) romanechite standard No. 34, 41% intensity. In this and subsequent figures the standard number refers to Table 1 in Potter and Rossman (1979c); (B) difference spectrum of C and D, 100% intensity; (C) unextracted dendrite, 100% intensity; (D) extracted dendrite, 51% intensity.

ing difference spectrum (Fig. 1B) is that of the manganese and iron oxides in the sample. For desert varnish samples, where Mn and Fe are present in comparable concentrations, features attributable to both manganese and iron oxide are present. The other deposits studied are either free of Fe or have it in sufficiently lower concentration than Mn that it does not interfere with the determination of manganese oxide mineralogy. We used a scanning electron microscope equipped with an energy-dispersive X-ray analyzer for semi-quantitative chemical analyses. X-ray powder diffraction was done with a Debye-Scherrer camera using vanadium-filtered chromium radiation.

Results

Desert varnish

The results of a detailed study of samples 1-3 (Table 1) have been reported elsewhere (Potter and Rossman, 1977, 1979a). The additional varnish samples listed in Table 1 confirm the generality of those results. Desert varnish invariably consists of birnesite in intimate mixture with hematite and large amounts of clay minerals. The clays are generally of the illite-montmorillonite type with minor kaolinite, but in several samples this concentration ratio is reversed.

Manganese dendrites

We define manganese dendrites as those manganese oxide concentrations which exhibit a dendritic pattern. They may be within the rock matrix (internal), along fracture surfaces of the rock, or on its surface.

Ring-structure manganese oxide minerals (Burns and Burns, 1977) are characteristic of all three types of manganese dendrites. With a single exception (No. 18) the manganese mineral present in the dendrites has been found to be romanechite ($\text{Ba}, \text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$ or one of the following hollandite-group minerals: hollandite, $\text{BaMn}_8\text{O}_{16}$; cryptomelane, $\text{KMn}_8\text{O}_{16}$; coronadite, $\text{PbMn}_8\text{O}_{16}$. Figures 1 and 2 are representative of the spectral data on which mineralogical identification is based, although generation of difference spectra was not necessary in all cases. We used chemical analysis to distinguish different hollandite-group minerals because their infrared spectra are identical in the 4000 cm^{-1} to 200 cm^{-1} region. Distinguishing features between the romanechite of Figure 1 and the hollandite of Figure 2 are the position of band near 700 cm^{-1} , the relative intensity of the band near 600 cm^{-1} (which is

Table 1. Sample information

Deposit type	#	Locality	Mn mineralogy Accessory mineralogy	Chemistry	Description
desert varnish	1	Four Buttes, Ca.	birnessite I-M/Hem,Kao//Qtz	-	coating on andesite boulders
	2	Salt Spring, Ca.	birnessite I-M/Hem,Kao//Qtz	-	coating on small quartzite outcrop
	3	Stoddard Wells, Ca.	birnessite I-M/Hem,Kao//Qtz	-	coating on desert pavement rhyolite and quartz cobbles
	4	Little Colorado Cyn., Az.	birnessite Kao/I-M//Qtz	-	streaked "stain" coating quartz conglomerate canyon walls
	5	Biklabito, N.M.	birnessite* [†] I-M/Hem,Kao//Qtz	-	coating on small sandstone outcrop and desert pavement dacite porphyry cobbles
	6	Petroglyph Park, N. M.	birnessite* [†] I-M/Kao//	-	coating on basalt outcrop
	7	Thunderbird Park, Az.	birnessite I-M/Hem,Kao//Qtz	-	coating on desert pavement basalt cobbles
	8	Funeral Peak, Ca.	birnessite* [†] I-M/Kao,Qtz// ⁺	-	coating on colluvial gneiss and hornfels cobbles
	9	Ojo Cyn., Az.	birnessite* [†] I-M/Kao//Qtz	-	coating on alluvial limestone cobbles
	10	Cady Mtn., Ca.	birnessite I-M/Kao//Qtz	-	coating on desert pavement volcanic rock cobbles
	11	Lake Pleasant, Az.	birnessite I-M/Kao//	-	coating on small banded iron formation outcrop
	12	Eatza Mtn., Nev.	birnessite* [†] I-M/Kao//	-	coating on basalt boulders
	13	Negev Desert, Israel	birnessite Kao/Hem,I-M/Qtz	-	coating on chert artifact in desert pavement
	14	Fort Davis, Tx.	birnessite* [†] I-M/Kao,Qtz// ⁺	-	coating on basalt cobble
manganese dendrites	15	Soda Mtns., Ca.	coronadite none	Mn,Pb/Ca//Zn,Cu,Al,Si,Fe	surficial dendrites up to 1 mm thick on alluvial sandstone cobble
	16	Southwestern United States	cryptomelane Kao/Cbn,Qtz	Mn/K,Ca//Si,Al,Fe	internal dendrites < 100 μm thick in felsite
	17	South Dakota	romanechite I-M/Kao,Qtz,Fld//	Mn,Si,Ba/Al,Ca//Mg,Pb, Fe,Na	fracture surface and internal dendrites < 100 μm thick on pegmatitic feldspar
	18	Pala, Ca.	todorokite /Kao//	Mn,Si,Al/Ca,Ti//Fe,K,Pb	surficial and internal dendrites up to 1 mm thick on pegmatite
	19	Barstow, Ca.	romanechite Cla/CaI,Qtz//	Ca,Mn,Si/Ba//K,Mg,Al	fracture surface dendrites up to 1 mm thick on siltstone outcrop
	20	Argus Peak, Ca.	hollandite Qtz/Kao	Mn,Si,Ba/K//Ca,Al,Pb	internal dendritic stain in siltstone outcrop
	21	Afton Canyon, Ca.	hollandite Cbn,Ser//	Mn,Si,Mg/Al,Ba//Ca	internal dendritic stain in calcareous claystone alluvial boulder
	22	Cady Mtn., Ca.	romanechite //Qtz	Mn,Ba//Si,Ca,K	surficial dendrites up to 1 mm thick on alluvial volcanic rock
	23	Beechworth, Australia	cryptomelane Kao//Qtz	Mn/K//Ba,Si,Al,Mg	surficial dendrites up to 1 mm thick on granite
	24	Oro Preto, Brazil	hollandite I-M//	Mn/Ba/K,Al,Si//Ca	internal dendrites < 100 μm thick in micaceous lamellae of quartz mica schist
cave deposits	25	Southeastern United States	birnessite //Qtz,Cla	Mn,Fe,Ca/Si//K,Ba	veins of purer material in concretions of oxide and clay from a dry streambed
	26	Southeastern United States	birnessite /Kao,I-M,Qtz//	Mn,Si,Fe,Ca/Cl,Al//Mg,Na	coating on pebbles of varied lithology from a dry streambed
stream deposits	27	Ladysmith, Wis. (Flambeau R.)	birnessite /Cla,organics//	Si,Mn,Fe,Al/Ca,Mg//	coating < 100 μm thick on streambed quartzite cobbles
	28	Athens, Ga. (Turkey Cr.)	birnessite /Kao/organics	Mn,Fe/Ca//Al,Si/Ni,Ba	coating < 100 μm thick on streambed gneiss cobbles
	29	Pilar, N.M. (Rio Grande R.)	birnessite I-M/Kao,Nit//	Si,Al,Mn,Ca,Fe//Ti,K,Mg	coating < 100 μm thick on basalt cobbles in splash zone
	30	Long Pond Quad., Me. (Pyrite Cr.)	nanite none	Mn//Al,Ba,Si,Ca,K,Fe	concretions in stream alluvium
	31	The Forks Quad., Me. (Shawm Cr.)	birnessite /I-M,Qtz//	Mn,Si,Al,Fe/Ca//K,Zn	concretions in stream alluvium
	32	Montezuma, Col. (Deer Cr.)	birnessite /Kao//	Mn/Si,K//Al	mountain-side deposit probably associated with a spring
miscellaneous samples subglacial deposit	33	Jackson Glacier, Mont.	birnessite or todorokite Qtz//Chl	Si,Al,Mn,Fe,Mg/Ca,K//	coating < 100 μm thick on siltstone outcrop surface under glacier
	34	Khumbu Region, Nepal	birnessite or todorokite* [†] none	Si,Al,Fe,Mn/K,Ti,Ca//Mg	coating < 100 μm on siltstone outcrop surface under glacier
crack deposit	35	Sierra Natl. Forest, Ca.	romanechite + ? Kao/Qtz//	Mn,Si,Al//K,Ca,Mg,Fe	coating up to 1 mm thick on granite outcrop near a water seep
	36	Cady Mtns., Ca.	hollandite + romanechite /Qtz//	Mn,Ba/Si,Al,Mg//K	coating up to 1 mm thick on volcanic rock outcrop
counterfeit Mn deposits	37	Sierra Natl. Forest, Ca.	none organic//	-	coating up to 1 mm thick on granite outcrop in a water seep
	38	Rock Creek, Ca.	none organic//	-	coating up to 1 mm thick on granite boulders in stream splash zone
	39	Summit Meadow Lk., Ca.	none iron oxide//	Fe/Al,Mn,Si//	coating up to 1 mm thick on granite in lake outlet streambed
	40	Meteor Crater, Az.	none organic//	-	dendritic growth on shocked sandstone
	41	Antarctica	none	-	polished surface of hornfels which has the appearance of desert varnish

*The following abbreviations are used: I-M = illite-montmorillonite mixed-layer clay, illite, or muscovite, which are nearly indistinguishable by infrared spectroscopy; Kao = kaolinite; Hem = hematite; Qtz = quartz; Cbn = carbonate; Fld = feldspar; Cla = unidentified clay mineral; Ser = serpentine; Nit = nitrate; Chl = Chlorite. The symbols / and // are used to indicate roughly the relative amounts of accessory minerals and of chemical elements. Accessory minerals listed to the left of a single slash are present in such high concentration that they dominate the infrared spectrum. Accessory minerals to the right of a double slash are in sufficient concentration that they significantly affect the spectrum. Accessory minerals to the left of the double slash are detected by infrared spectroscopy but are present in too low a concentration to significantly alter the spectrum. Chemical elements to the right of a double slash are the dominant constituents; those between single and double slashes are minor constituents; those to the right of a double slash are trace constituents. This is based roughly on peak height from the energy dispersive X-ray detector without any quantitative corrections. More detailed descriptions and sample localities are found in Appendix B, Potter (1979).

*†Noise introduced by the generation of difference spectra is too large to allow determination of manganese mineralogy. Instead, it is inferred from direct comparison to other spectra of the same phenomenon with similar accessory minerals.

+An iron oxide phase is present. Its mineralogy was not determined, but it is presumed to be hematite on the basis of color.

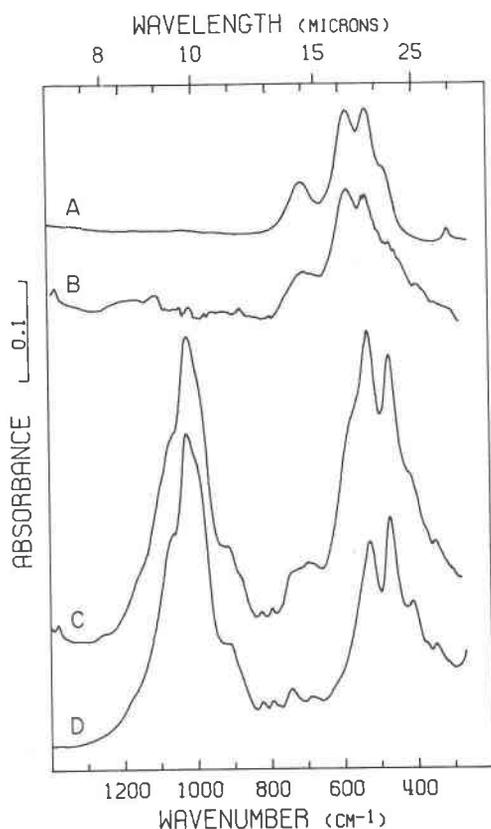


Fig. 2. Infrared spectra identifying hollandite-group mineral in manganese dendrite No. 24: (A) cryptomelane standard No. 28, 28% intensity; (B) difference spectrum of C and D, 100% intensity; (C) unextracted dendrite, 100% intensity; (D) extracted dendrite, 75% intensity.

prominent in the hollandite-group minerals and only a shoulder in romanechite), and the presence of the weak band near 450 cm^{-1} for romanechite. In addition, romanechite has H_2O absorption bands at 3520 cm^{-1} , 3470 cm^{-1} , and 1605 cm^{-1} (Fig. 7), which distinguish it from all other manganese oxides. Our chemical data (Table 1) show high Ba concentrations in those samples with romanechite mineralogy and thereby support the infrared results. The single example of a non-channel structure manganese oxide, No. 18, was unambiguously identified as todorokite, $(\text{Mn,Ca,Mg})\text{Mn}_3\text{O}_7 \cdot \text{H}_2\text{O}$ (Fig. 3). We have found no dendrites with pyrolusite mineralogy. The general term "pyrolusite dendrite" is a misnomer and should be discontinued.

Manganese dendrites have no characteristic accessory mineralogy such as the high concentration of clay minerals in desert varnish. Some dendrites are nearly pure manganese oxide. In others the manganese oxide is mixed with various carbonate or silicate minerals characteristic of the weathering environment. These accessory minerals are not

necessarily involved in the dendrite formation process. The fracture-surface dendrites of sample No. 17 appear to be a local staining of clay minerals present throughout the fractures. Accessory minerals of the internal dendrites are in many cases simply the minerals of the rock matrix in which the dendrites have formed.

Manganese dendrites do not generally have a high degree of chemical homogeneity. The manganese concentration varies greatly throughout the stained area in those dendrites which are not pure oxide. In most dendrites areas tens of microns in size can be found which are predominantly manganese oxide. The chemical analyses in Table 1 are from these areas. In other areas the dendrite chemistry is dominated by the accessory minerals. Manganese dendrites appear to be manganese oxide coatings on a substrate composed of the accessory minerals. We have found only trace quantities of Fe in manganese dendrites. This distinguishes them from other manganese concentrations, which generally contain Fe as one of the major constituents.

Stream deposits

Our stream deposit samples include coatings on stones from both the streambed and the splash zone, and concretions from stream alluvium. The dominant manganese mineralogy of these samples is birnessite, $(\text{Na,Ca,K})\text{Mn}_7\text{O}_{14} \cdot 3\text{H}_2\text{O}$. Figure 4 is representative of the spectral data on which this mineralogical identification is based. The two intense, poorly resolved bands near 500 cm^{-1} are

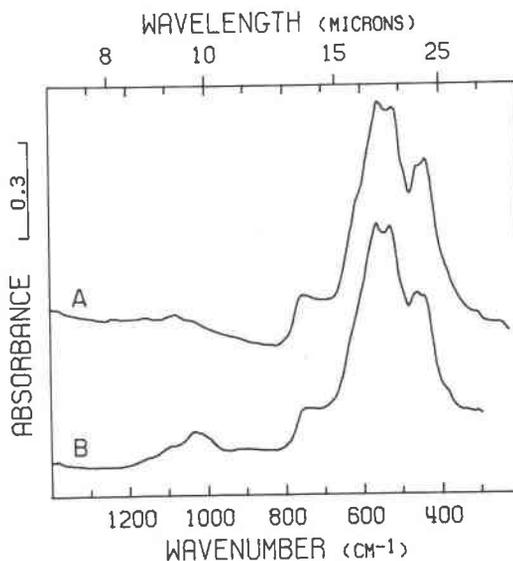


Fig. 3. Infrared spectra identifying todorokite in manganese dendrite No. 18: (A) todorokite standard No. 55, 136% intensity; (B) unextracted dendrite, 100% intensity.

characteristic of birnessite and distinguish it from all other manganese oxides (Potter and Rossman, 1979c), although it is easily confused with some todorokite samples. Most todorokites have spectra distinct from that of Figure 4C (Fig. 3A for example), but the spectrum of highly disordered todorokite (Fig. 4A) is similar. The nearly equal intensity of the two major absorption bands of Figure 4C and the positions of the weak shoulders at higher wave number indicate a birnessite rather than a todorokite mineralogy. Qualitative chemical analyses of the river deposits support a birnessite mineralogy. Invariably Ca and/or K are present in minor amounts. Nowlan (1976) has found birnessite in one stream in Maine and noted that many samples from his other Maine localities (among which are our samples No. 30 and 31) have the two broad X-ray lines characteristic of δ - MnO_2 , which is thought to be a disordered birnessite (Buser *et al.*, 1954).

We have identified sample No. 31 as nsutite, $Mn(O,OH)_2 \cdot xH_2O$, on the basis of its infrared spectrum (Fig. 5) and chemistry. The spectrum of sample No. 31 is characteristic of nsutite in the broadness of its band near 580 cm^{-1} and in the positions of the weak bands at energies lower than 400 cm^{-1} . However, the reliability of identification on this basis alone is questionable because of the strong similarity between the infrared spectra of sample No. 31 and the hollandite-group minerals. Qualitative chemical analysis which indicates only traces of cations other than Mn confirms the nsutite mineralogy. Because of differences in cation absorption properties, this mineralogical difference may have profound effects on the use of trace elements in manganese oxides for geochemical exploration.

Stream deposits do not, in general, exhibit the high degree of separation of manganese from iron seen for the manganese dendrites. We found Fe to be a major constituent of many of the stream samples. More extensive chemical analyses (Carpenter *et al.*, 1975; Nowlan, 1976) indicate that this is generally true for Turkey Creek, Pyrite Creek, and Shawn Creek. Nowlan's report of nearly equal amounts of Mn and Fe in Pyrite Creek deposits represents the average composition; our analyses are of the manganese-rich areas.

Cave deposits

The two cave deposits examined are both predominantly birnessite and resemble the river deposits in all respects, which is not surprising since they came from dry streambeds in caves. Birnessite and romanechite have previously been reported from

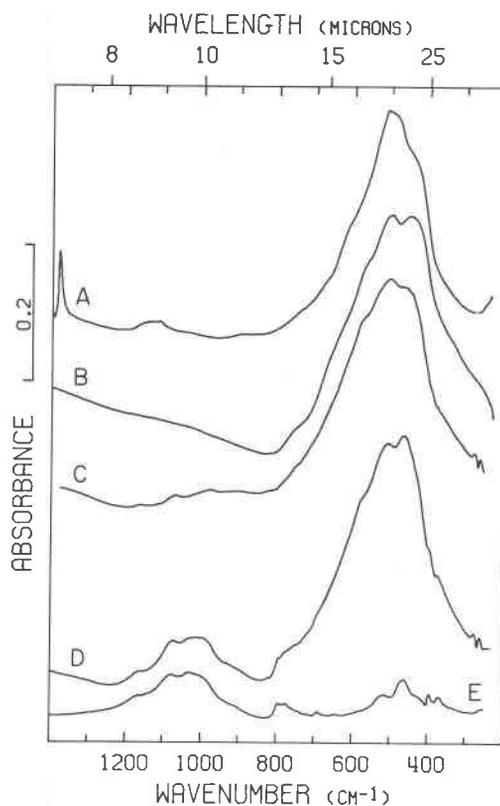


Fig. 4. Infrared spectra identifying birnessite in stream deposit No. 31: (A) disordered todorokite standard No. 57, 120% intensity; (B) birnessite standard No. 47, 100% intensity; (C) difference spectrum of D and E, 100% intensity; (D) unextracted deposit, 100% intensity; (E) extracted deposit, 14% intensity.

caves (Moore and Nicholas, 1964), where they form coatings on stream cobbles and soot-like layers on walls and other cave surfaces.

Miscellaneous

Subglacial manganese deposits: We have examined samples from two areas where a receding glacier has exposed bedrock surfaces stained with manganese oxides. The infrared spectrum of the manganese oxide is attributable to either a disordered birnessite or a disordered todorokite (Fig. 6). The latter is a better match, although the intensity of the lower-energy birnessite band is variable. We suggest (Potter and Rossman, 1979c) that birnessite and todorokite disorder to the same structural entity. If this suggestion is correct, a continuum exists between the two structures, and as disorder increases the distinction between the two minerals becomes meaningless. Except for a slight increase in the amount of chlorite, the bulk of the stained material does not differ from the rock matrix, which is predominantly quartz. In both samples Fe, probably as iron oxide, is a major constituent. It appears that

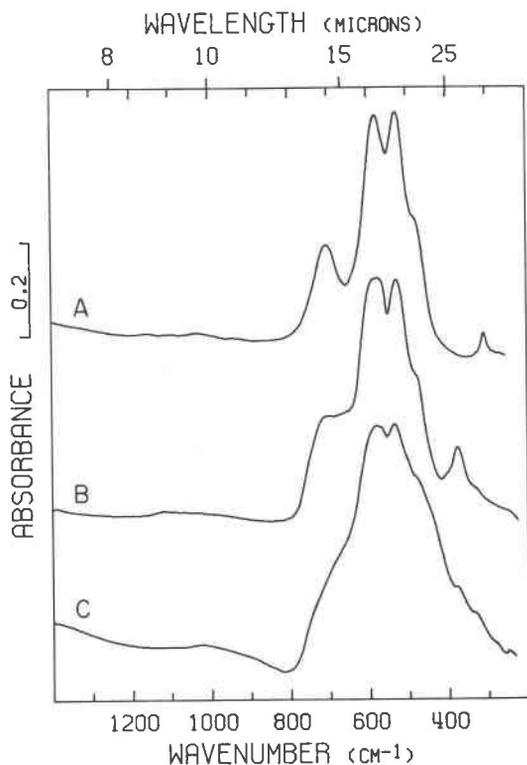


Fig. 5. Infrared spectra identifying nsutite in river deposit No. 30: (A) cryptomelane standard No. 28, 110% intensity; (B) nsutite standard No. 16, 88% intensity; (C) unextracted river deposit, 100% intensity.

the manganese oxide is deposited on the rock in relatively pure form.

Crack deposits: The two manganese crack deposits we have examined resemble manganese dendrites in manganese mineralogy, accessory mineralogy, and iron content. We have too few samples to generalize from these results. These crack deposits formed at unknown depth within the rock, and should be distinguished from more surficial crack deposits which have formed within the upper few centimeters of the crack in association with desert varnish at the surface and iron oxide-clay deposits deeper in the crack. The appearance and association of these latter deposits suggests that they resemble desert varnish in mineralogy and composition.

Counterfeit manganese deposits: Polished surfaces, organic matter, and iron oxide with traces of manganese oxide can each give the appearance of a manganese oxide stain. Although careful field examination can generally distinguish these phenomena from manganese concentrations, it is sometimes necessary to ascertain the presence of manganese oxide by laboratory tests. Several examples are listed in Table 1.

Conclusions

Our results indicate that distinctions between manganese oxide concentrations based on their morphologic relations in the terrestrial weathering environment have a sound basis in terms of the mineralogy of the manganese oxides and their accessory minerals. Desert varnish, manganese dendrites, and stream deposits each have a characteristic mineralogy which reflects their different morphologies and environments. Desert varnish is composed predominantly of illite-montmorillonite and kaolinite clay minerals with lesser and somewhat variable amounts of hematite and birnessite. In manganese dendrites, the manganese is generally present as romanechite or a hollandite-group mineral and is sometimes the major constituent of the dendrites. The accessory silicate mineralogy is variable, and iron oxide is present in only minor amounts. Manganese oxide of a birnessite mineralogy is the dominant phase in manganese stream deposits, but minor iron oxide and clay min-

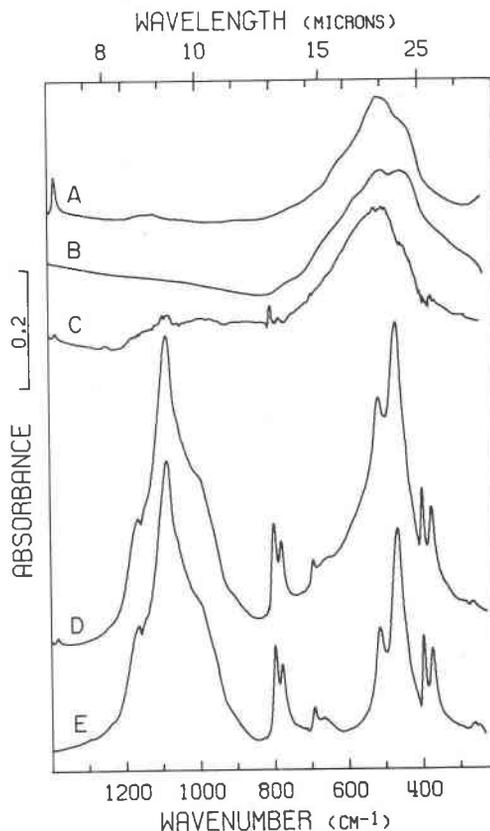


Fig. 6. Infrared spectra identifying birnessite in subglacial deposit No. 33: (A) disordered todorokite standard No. 57, 75% intensity; (B) birnessite standard No. 47, 60% intensity; (C) difference spectrum of D and E, 100% intensity; (D) unextracted subglacial deposit, 100% intensity; (E) extracted subglacial deposit, 53% intensity.

erals are generally present. The diverse mineralogy previous workers have reported for manganese soil concretions (Taylor *et al.*, 1964; Gallaher *et al.*, 1973; McKenzie, 1977; Ross *et al.*, 1976; Potter and Rossman, 1979b) contrasts with desert varnish, manganese dendrites, and stream deposits. This reflects the wide range of environmental conditions possible in soils. Data on several subglacial deposits and crack deposits suggests that the former resemble river deposits, and the latter resemble manganese dendrites. This is reasonable in terms of the environmental conditions.

The characteristic differences may reflect differences in the formation mechanisms of the manganese deposits and are therefore useful in further understanding these mechanisms. The variable mineralogy and quantity of manganese-dendrite accessory minerals and their frequent similarity to minerals of the rock matrix argue strongly that they are simply passive contaminants. We can rule out several of the possible factors which might control a romanechite vs. hollandite-group mineralogy in manganese dendrites. The presence of Ba does not direct the mineralogy to romanechite, as evidenced by the presence of hollandite in three dendrites. Rock lithology shows no correlation with mineral species, nor does

the relation of the dendrite to the rock (internal, fracture surface, or surficial). Romanechite is stable to conversion to hollandite up to at least 400°C (Fleischer, 1960), so that thermal history, except as it may influence primary mineralogy, is probably not an important factor in this regard. The relation between romanechite and hollandite is a closer one than distinct mineral names might suggest. Turner and Busch (1979) have shown that intergrowth occurs between the two minerals at the level of the unit cell and have explained variations in romanechite X-ray diffraction patterns on that basis. Several of our samples have infrared spectra intermediate between those of romanechite and hollandite (Fig. 7). This may be the result of intimate structural intergrowth, although it could be explained by an intimate physical mixture. We found no evidence for mixed phases under the scanning electron microscope. The intensities of the water absorption bands in the 4000 cm^{-1} to 1400 cm^{-1} do not follow the trend set by the absorption bands in the 1400 cm^{-1} to 200 cm^{-1} region, which are due to vibrations of the ring framework of MnO_6 octahedra. This reflects the variable amounts of water in romanechite and suggests that water is not important in controlling the mineralogy.

At the Cady Mountain locality we found desert

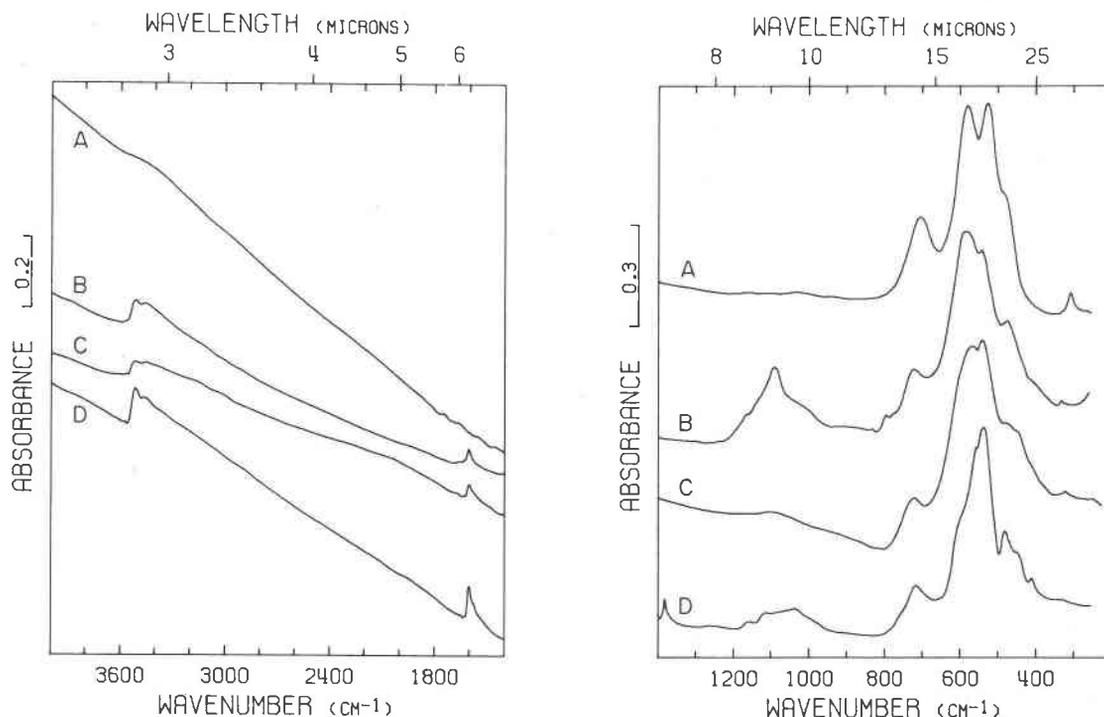


Fig. 7. Infrared spectra illustrating the range between pure romanechite and pure hollandite structures: (A) cryptomelane (hollandite-group) standard No. 28, 90% intensity; (B) creek deposit No. 36, difference spectra at 105% intensity (minor quartz absorption removed); (C) manganese dendrite No. 22, 94% intensity; (D) romanechite standards No. 38 (4000 cm^{-1} –1400 cm^{-1}) and No. 34 (1400 cm^{-1} –200 cm^{-1}), 100% intensity.

varnish (No. 10) and crack deposits (No. 36) developed within a meter of each other. Several meters away were manganese dendrites (No. 22). The varnish has birnessite, and the crack deposit and dendrites are romanechite-hollandite intergrowths (Fig. 7). Clay minerals are not detectable in either the crack deposit or the dendrites. It is not known how far below the ground surface or at what time the crack deposits and dendrites formed, but the occurrence in close proximity of manganese oxide concentrations which differ markedly in mineralogy suggests that the accessory clay minerals may be an important factor in controlling manganese oxide mineralogy. Although the presence of clay minerals is not a sufficient condition for birnessite formation (some manganese dendrites have appreciable clay associated with hollandite or romanechite), it appears to be necessary. Clay minerals are an integral part of desert varnish, which invariably has birnessite. All stream deposits with birnessite mineralogy are associated with clay minerals. The only stream deposit lacking clay minerals is the nsutite from Pyrite Creek. Environmental conditions do not appear to be responsible for the distinctive mineralogy of the Pyrite Creek deposit. The Shawn Creek deposit has the normal birnessite mineralogy. These two streams are within 20 km of each other in western Maine and differ only in water trace-element chemistry (Nowlan, 1976). Pyrite Creek water is anomalously high in Pb and Zn, but we know of no reason why this should lead to nsutite formation.

Burns and Burns (1977) have suggested that epitaxial growth on iron oxides may be responsible for the occurrence in marine manganese nodules of δ -MnO₂, which is believed to be a disordered birnessite. With the exception of some birnessite soil concretions (Taylor *et al.*, 1964), there is a good correlation between birnessite mineralogy and iron content in manganese oxide deposits of the terrestrial weathering environment.

Infrared spectroscopy has provided mineralogical information on deposits which are too poorly crystalline, too finely particulate or too highly contaminated with other crystalline phases for successful study by X-ray diffraction. It is hoped that infrared spectroscopy will find wider application to more detailed investigation into the genetic nature and relationships of the various manganese oxide concentrations.

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References

- Burns, R. G., and V. M. Burns (1977) Mineralogy. In G. P. Glasby, Ed., *Marine Manganese Deposits*, p. 185-248. Elsevier, Amsterdam.
- Buser, W., P. Graf and W. Feitknecht (1954) Beitrag zur Kenntnis der Mangan(II)-manganite und des δ -MnO₂. *Helvetica Chim. Acta*, 37, 2322-2333.
- Carpenter, R. H., T. A. Pope and R. L. Smith (1975) Fe-Mn oxide coatings in stream sediment geochemical surveys. *J. Geochem. Explor.*, 4, 349-363.
- Fleischer, M. (1960) Studies of manganese oxide minerals. III. Psilomelane. *Am. Mineral.*, 45, 176-187.
- Gallaher, R. N., H. F. Perkins, K. H. Tan and D. Radcliffe (1973) Soil concretions: II. Mineralogical analysis. *Proc. Soil Sci. Soc. Am.*, 37, 469-472.
- McKenzie, R. M. (1977) The manganese oxides and hydroxides. In J. B. Dixon, Ed., *Minerals in Soil Environments*, p. 181-193. Soil Science Society of America, Madison, Wisconsin.
- Mehra, O. P. and M. L. Jackson (1960) Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. In A. Swineford, Ed., *Proc. Seventh Natl. Conf. Clays and Clay Miner.*, p. 317-327. Pergamon, Oxford.
- Moore, G. W. and G. Nicholas (1964) *Speleology*. D. C. Heath and Company, Boston.
- Nowlan, G. A. (1976) *Genesis of manganese-iron oxides in stream sediments in Maine*. U.S. Geol. Surv. Open-File Report 76-878.
- Potter, R. M. (1979) *The tetravalent manganese oxides: clarification of their structural variations and relationships and characterization of their occurrence in the terrestrial weathering environment as desert varnish and other manganese oxide concentrations*. Ph.D. Thesis, California Institute of Technology, Pasadena, California.
- and G. R. Rossman (1977) Desert varnish: the importance of clay minerals. *Science*, 196, 1446-1448.
- and — (1979a) The manganese and iron oxide mineralogy of desert varnish. *Chem. Geol.*, 25, 79-94.
- and — (1979b) A magnesium analogue of chalcophanite in manganese-rich concretions from Baja California. *Am. Mineral.*, 64, 1227-1229.
- and — (1979c) The tetravalent manganese oxides: identification, hydration, and structural relationships by infrared spectroscopy. *Am. Mineral.*, 64, 1199-1218.
- Ross, Jr., S. J., D. P. Franzmeier and C. B. Roth (1976) Mineralogy and chemistry of manganese oxides in some Indiana soils. *Proc. Soil Sci. Soc. Am.*, 40, 137-143.
- Taylor, R. M., R. M. McKenzie and K. Norrish (1964) The mineralogy and chemistry of manganese in some Australian soils. *Aust. J. Soil Res.*, 2, 235-248.
- Turner, S. and P. R. Buseck (1979) Some manganese oxide tunnel structures and their intergrowth. *Science*, 203, 456-458.