

A magnesium analogue of chalcophanite in manganese-rich concretions from Baja California

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Abstract

Concretions which carry chemical remanent magnetization in sediments in Baja California, Mexico, previously called "hydropsilomelane," were found to consist of siltstone matrix minerals cemented by a manganese oxide. The X-ray powder pattern, infrared spectra, and chemical analyses indicate that the manganese oxide has the chalcophanite structure. The high concentration of magnesium, presumed to occur in the interlayer position of this mineral, suggests that it is the magnesium analogue of chalcophanite and extends the known range of substitution in chalcophanite-structure minerals.

In a study of the chemical remanent magnetization of sediments in Baja California, Larson and Walker (1975) reported the presence of manganese-rich concretions which were found to carry remanent magnetization in numerous sedimentary horizons. They informally named the manganese oxide phase "hydropsilomelane" due to similarities in both chemistry and X-ray diffraction pattern to the manganese oxide romanechite (psilomelane). We studied these concretions as part of a survey concerned with the mineralogy of manganese oxides in the terrestrial weathering environment (Potter and Rossman, 1979b).

Samples for infrared and qualitative chemical analysis are from a locality 56 km south of San Felipe, Baja California, Mexico, and consist of weakly cemented siltstone in which the concretions are dispersed. The siltstone was disaggregated by immersion in water and the concretions hand-picked from the coarse fraction of the sediment. Removal of the manganese by chemical extraction (Mehra and Jackson, 1960) showed that the bulk of the concretions consist of the siltstone matrix minerals calcite, quartz, clay, and mica. This is in agreement with the infrared spectra of whole concretions (Fig. 1) obtained by methods previously reported (Potter and

Rossman, 1977). Its spectrum is dominated by absorption due to the siltstone matrix minerals.

In order to investigate the manganese oxide mineralogy, powdered concretions were washed with 1.0M acetic acid to remove the calcite, and difference infrared techniques developed previously (Potter and Rossman, 1979a) were then applied to produce infrared spectra of the pure manganese oxide phase of the concretions. In the 4000 cm^{-1} to 1400 cm^{-1} region of the spectrum, absorption due to the hydrous components of the manganese oxide can be seen without interference from the contaminating silicates, and strongly suggests a chalcophanite structure based on comparison to standard chalcophanite and aurorite spectra (Fig. 1). Absorption in the 1400–200 cm^{-1} region confirms that the manganese oxide has the chalcophanite structure. The positions and number of absorption bands in Figure 1 are diagnostic for minerals with the chalcophanite structure (Potter and Rossman, 1979c). Two such minerals are known, chalcophanite and aurorite. These differ in the nature of the cations between the layers of manganese octahedra, but are indistinguishable on the basis of their X-ray diffraction and infrared absorption patterns. Chemical analysis of manganese-rich areas of the concretions by energy-dispersive X-ray analysis under a scanning electron microscope indicated Mn as a major component with lesser amounts of Si, K, Ca, Al, Mg, and Na. We could find no areas as rich in oxide as those analyzed by Larson and Walker.

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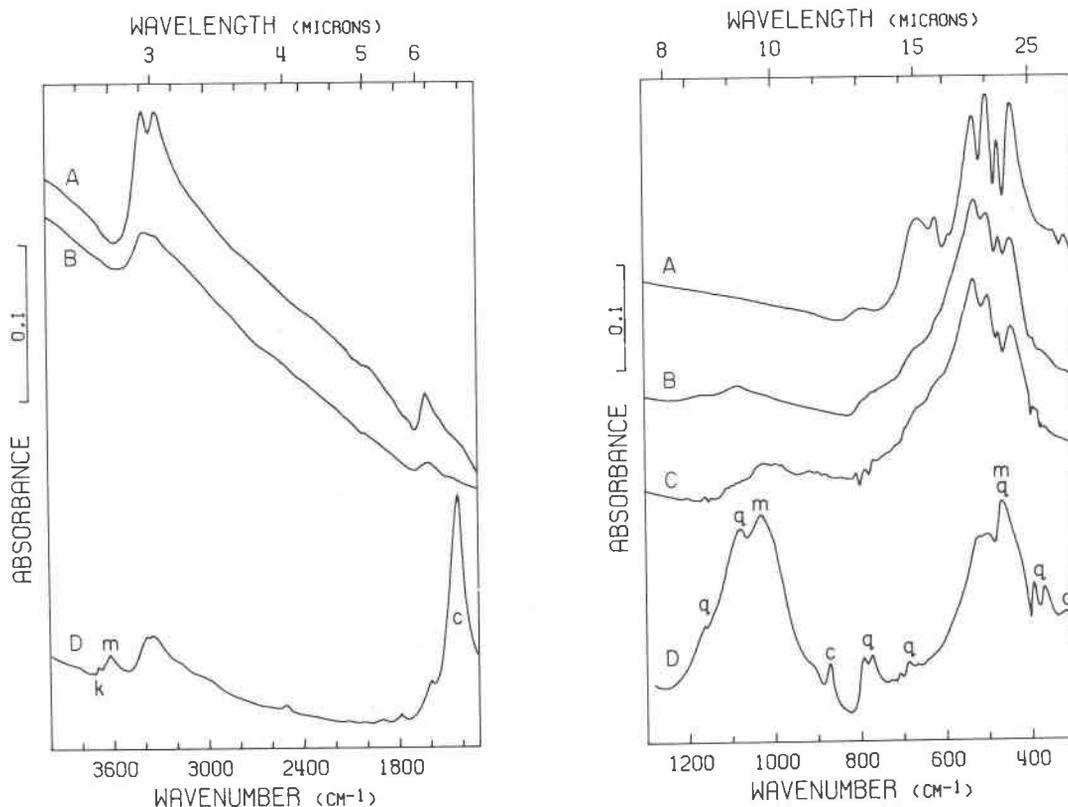


Fig. 1. Infrared spectra of concretions compared to reference manganese oxide spectra. Reference spectra of chalcophanite (A) and aurorite (B). The spectrum of the whole concretion (D) shows bands attributable to calcite (c), mica (m), kaolinite (k), and quartz (q), in addition to the manganese oxide. Extracted samples show that the overlapping pairs of bands in the 3200–3500 cm^{-1} region are free from interference from the other components. They indicate a chalcophanite-group manganese oxide. The spectrum of the manganese oxide phase in the 1300–300 cm^{-1} region, obtained in a difference spectrum (C), is similar only to chalcophanite-group manganese oxides.

The X-ray and chemical data of Larson and Walker (1975) are in agreement with our infrared results. Their X-ray data are a significantly better match to chalcophanite and aurorite than to romanechite (Table 1). Larson and Walker report that heating at 550°C caused the 6.92A peak to disappear and a new one to develop at 4.87A. This is strongly reminiscent of the behavior of chalcophanite on heating (Dasgupta, 1974), in which the 6.96A chalcophanite line disappears and an intense 4.76A line is produced. Larson and Walker's chemical data yield the following formula on the basis of 7 oxygens (excluding water) with all Mn in the +4 oxidation state:



This is in agreement with the formula of a magnesium analogue of chalcophanite, $\text{MgMn}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$, if allowance is made for uncertainty in water content, which was determined by difference of the micro-

probe analysis from 100 percent. If some manganese is present as Mn^{2+} , as seems probable from published chalcophanite analyses, the agreement would improve. This would increase the interlayer-site population, decrease the manganese octahedra layer-site population, and increase the water content. It is possible that the iron is not present in the manganese oxide, but occurs instead as a minor phase, in view of its low abundance in Larson and Walker's analysis and its absence in our analysis. The chemical data do not yield a recognizable romanechite formula when calculated on the basis of 10 non-water oxygens. The mutually supporting results of infrared spectroscopy, X-ray diffraction, and chemical analysis indicate that the manganese oxide in the concretions has the chalcophanite structure.

The phase which we are describing differs from all other previously reported minerals with the chalcophanite structure in the nature of the substitution

Table 1. X-ray diffraction data for chalcophanite, aurorite, "hydropsilomelane," and romanechite*

chalcophanite**		aurorite**		"hydropsilomelane"		romanechite**	
d(A)	I	d(A)	I	d(A)	I	d(A)	I
6.96	10	6.94	10	6.92	10	9.68	3
4.08	5	4.06	5			6.95	6
3.50	6	3.46	7	3.48	4	3.48	6
						3.32	3
						3.23	3
						2.88	4
2.57	4	2.76	3			2.42	3
		2.54	5			2.41	10
		2.45	4			2.37	5
		2.40	4	2.40	1	2.26	4
2.24	5	2.23	5	2.23	4	2.19	8
						2.15	4
		2.13	3			1.82	4
1.90	3	1.90	4	1.89	1		
		1.80	3				
1.60	5	1.56	5	1.59	1	1.56	3
1.43	3	1.43	5	1.38	2	1.42	3

* Data from the following sources: chalcophanite, J.C.P.D.S. File Card No. 15-807; aurorite, Radtke *et al.*, 1967; "hydropsilomelane", Larson and Walker, 1975; romanechite, J.C.P.D.S. File Card No. 14-627.

** Lines with intensity lower than 3 have been omitted.

for the interlayer cation. Our reformulation of the chemical data of Larson and Walker indicates that Mg^{2+} is the cation predominantly substituting for Zn^{2+} , although some Mn^{2+} is probably present. There is no evidence for any Zn^{2+} or Ag^+ in the structure. This lends support to the idea that wide compositional variations exist for chalcophanite (Radtke *et al.*, 1967). We suggest that variation in the nature of interlayer cations in minerals of the chalcophanite structure is sufficiently large to justify the designation of a chalcophanite group.

The paragenesis of this phase is different from that of other occurrences of manganese oxides with the chalcophanite structure, and may indicate a significantly larger range of occurrence than has previously been recognized. Chalcophanite-group minerals have been thought to be relatively rare and of secondary origin, associated with extensive manganese mineralization. In Baja California, this phase occurs as a primary mineral formed authigenically in silt deposits with no relation to any other manganese mineral-

ization (Larson and Walker, 1975). Larson and Walker suggest that these manganese concretions may be a common feature of continental playa sediments. Their report that the concretions carry remanent magnetization raises the question of whether the magnetism resides in the manganese oxide or in another component. If the magnetism originates from the manganese oxide, the study of the effect of interlayer cation substitution on the magnetic properties of chalcophanite-group minerals becomes a matter of importance to paleomagnetic investigations.

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