

Table of Wavenumbers - Manganese Oxides<sup>1</sup>

Mineral <sup>2</sup>	band #	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Pyrolusite		335-340	390-400	535-615	630-670	705-735									
Ramdehllite		270	377	476	523	597	592	~750	1640	3335	3389	~3520			
Roosite		375-380	476	515-530	565-590	685-730									
Mallardite		310-312	~470	523-531	570-583	706-713									
Bannochite		265-269	320-325	403-404	435-440	448-475	531-535	603	720-723	1607-1615	3467-70	3526-31			
Chalcophanite		319	344	437	474	496	530	591	622	688	805	1635	3315-16	3400	
Lithiophorite		427	474	544	605	~631	723	753	910	1015	~1100	3431			
Birnessite		246	330-360	420-460	485-525	555-575	620-660	740-755	1631-1645	3352	3385-3435	3545-50	(much variation in H <sub>2</sub> O region)		
Buserite		359-362	411-414	475-477	509-510	633									
Todorokite		243	305-310	379-388	429-441	457-459	488	508-518	549-554	590	617-635	748-763	1593-1601	1642-49	1685-87
Banalcite		425-456	494-506	623-633	670-681	1643-54	3200-25	3378-97	3546-76	3496-3502	(much variation in H <sub>2</sub> O region)				

List of band positions

Roosite	221, 246, 278, 312, 374, ~411, 444, 477, 515, 550, 611, ~660, 709, 948
Greentite	293, 325, 358, 497, 579, ~613, 995, 1027, 1931, 2013, ~2175, 2190, 2695, 2825, 3000
Bannochite	246, 351, 514, ~592, 617
Manganoite	346, 370, 445, 487, 594, 613, 627, 730, 1087, 1119, 1149, 2068, 2665, ~3400, ~3525
Manganosite	313, ~466, ~458
Buserite	214, 225, 245, 288, 341, ~377, ~400, 469, ~503, 586, 648, 669
Psittacinite	213, ~251, ~270, 289, ~335, 393, ~438, ~494, 519, 570, ~604, ~671
Quemalite	~238, 266, 297, 321, ~338, 391, 496, 591, 652, 836, 1046, ~3000

1. The range of variation among samples is recorded. All values are corrected for instrument error using water vapor lines as standards. All samples run as TlK pellets. Units are cm<sup>-1</sup>.

2. Both natural minerals and synthetic analogues are included in this table.

## APPENDIX A

Our work on the lower-valent manganese oxides is summarized in this appendix. Table 1A contains information on sample locality and purity. Figures 1A-8A are representative of the various manganese oxides listed in Table 1A. They were all obtained on TlBr pellets under the same conditions as the figures presented in the text. Where the corresponding spectrum in KBr differs significantly it is included in Appendix B. Spectra of samples in Table 1A not included in this appendix are contained in Appendix B as indicated in Table 1A.

Table 1A. Sample information<sup>1</sup>

sample #	locality	ident. #	ref. #	fig. #	x-ray	IR
70	Palos Verdes, Hills, Calif.	CIT 9461	2	1A	pure	pure
71	Cuyuna Range, Minnesota	NMNH 105004	3	2A, 16B	pure	pure
72	Talcville, New York	NMNH 113969	4	16B	pure	pure
73	Anadia, Portugal	NMNH 133850		16B		t,qtz
74	Langban, Sweden	CIT 9462		17B		pure
75	Synthetic	CIT 9463	5	3A, 17B	pure	pure
76	Synthetic	CIT 9618	6	17B	pure	pure
77	Sagamore Mine, Minnesota	CIT 6048		18B	t, imp	pure
78	Synthetic	CIT 9619	7	4A	pure	pure
79	Langban, Sweden	CIT 2400		19B	t, pyc	t, pyc
80	Synthetic	CIT 9620	8	5A, 19B	pure	pure
81	Tachgagalt, Morocco	LCM 13888		6A	pure	pure
82	Postmasburg, S. Africa	HAV 110400		20B		pure
83	Synthetic	CIT 9621	9	7A	t, pyr	t, pyr?
84	Langban, Sweden	CIT 3097		8A	pure	pure

1. The abbreviations and the criteria for X-ray purity are the same as for Table 1.

2. Mitchell and Corey, 1973.

3. Gruner, 1947

4. Segeler, 1959.

5. Synthetic method: Giovanoli et al., 1967.

6. Manganous manganic oxide from Diamond Shamrock Chemical Company; Baltimore, Maryland.

7. Synthetic method: The synthetic method of Wadsley (1950b) for psilomelane produced a pure manganite. It was subsequently found that the manganous manganate used was contaminated with hausmannite.

8. Manganous oxide from Diamond Shamrock Chemical Company; Baltimore, Maryland; 0.01% Fe, 0.5% MnO<sub>2</sub> by their analysis.

9. Manganese sesquioxide HPX from Diamond Shamrock Chemical Company; Baltimore, Maryland.

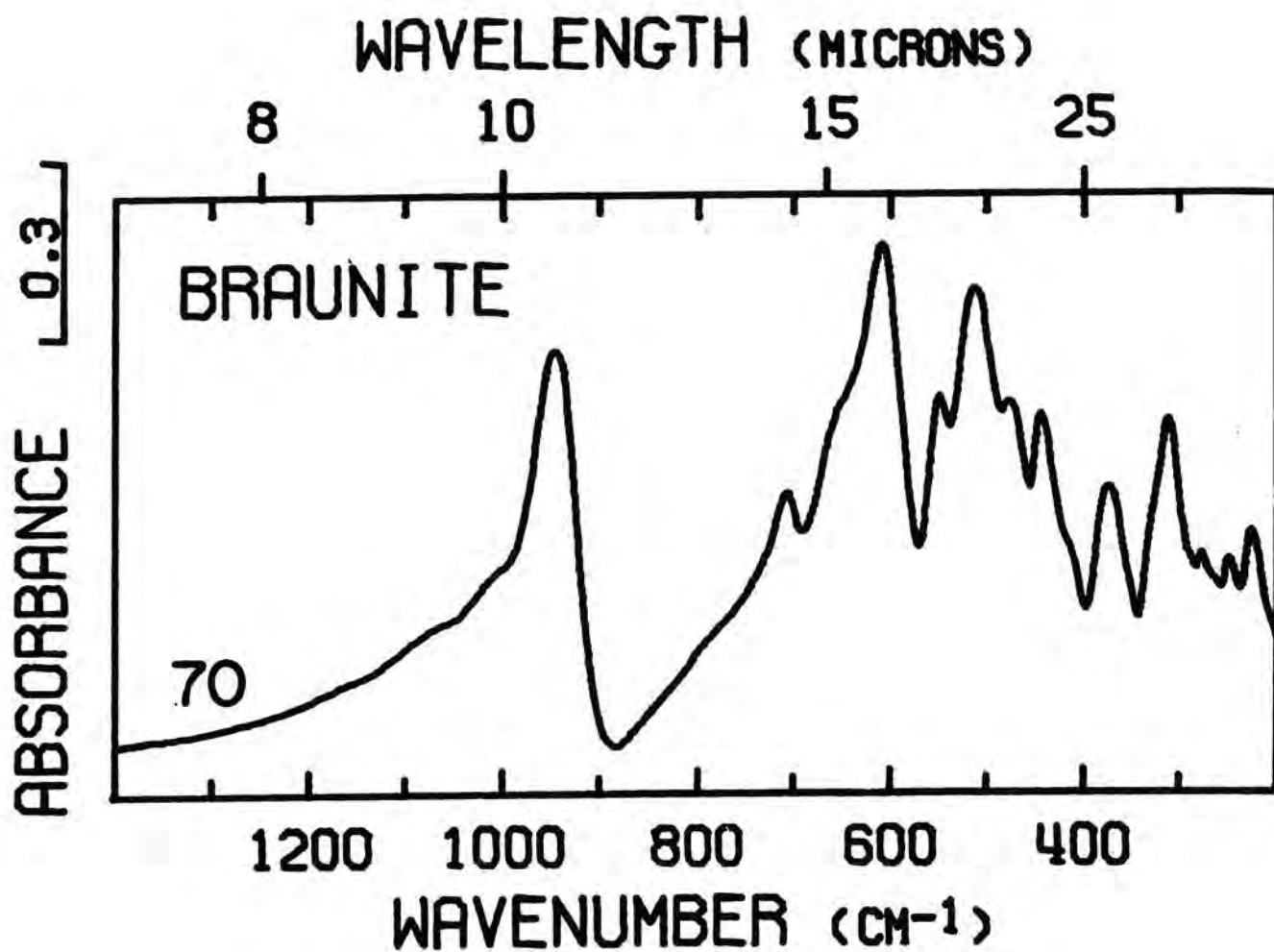


Figure 1A. Infrared spectrum of braunite. Presentation intensity: 344%.

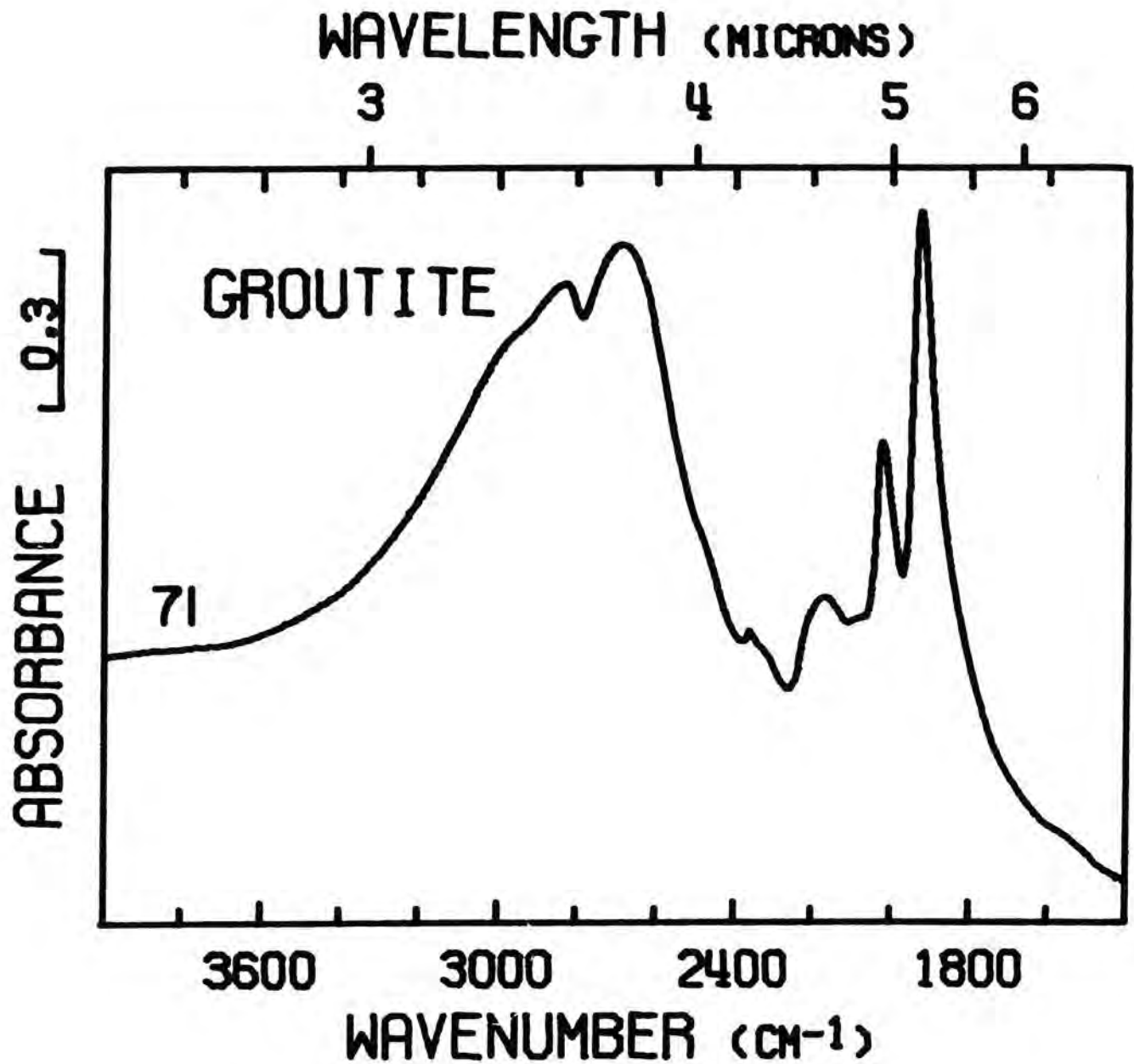


Figure 2A. Infrared spectrum of groutite. Presentation intensity: 268%. Figure continued on following page.

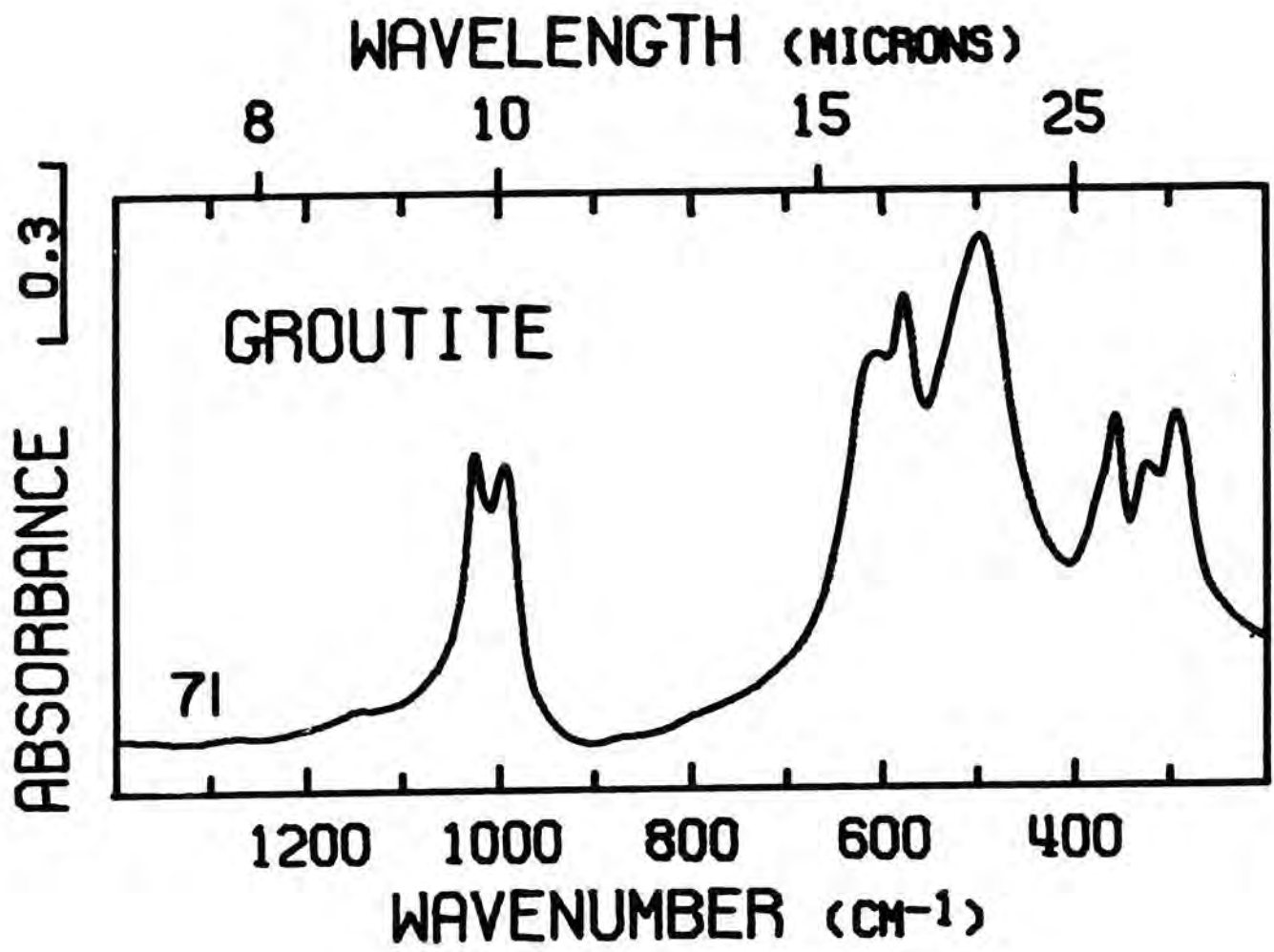


Figure 2A. Continued from preceding page.

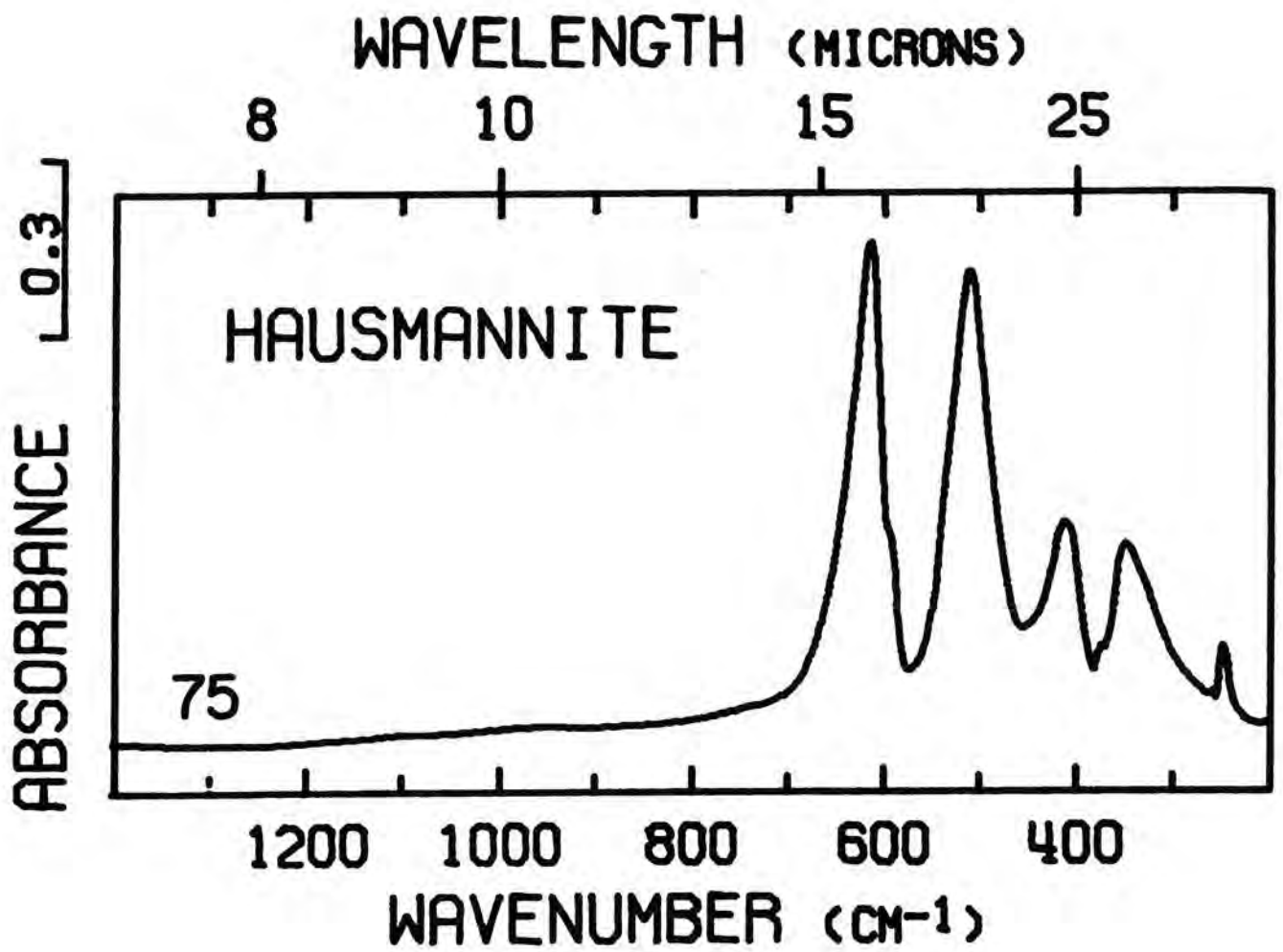


Figure 3A. Infrared spectrum of hausmannite. Presentation intensity: 182%.

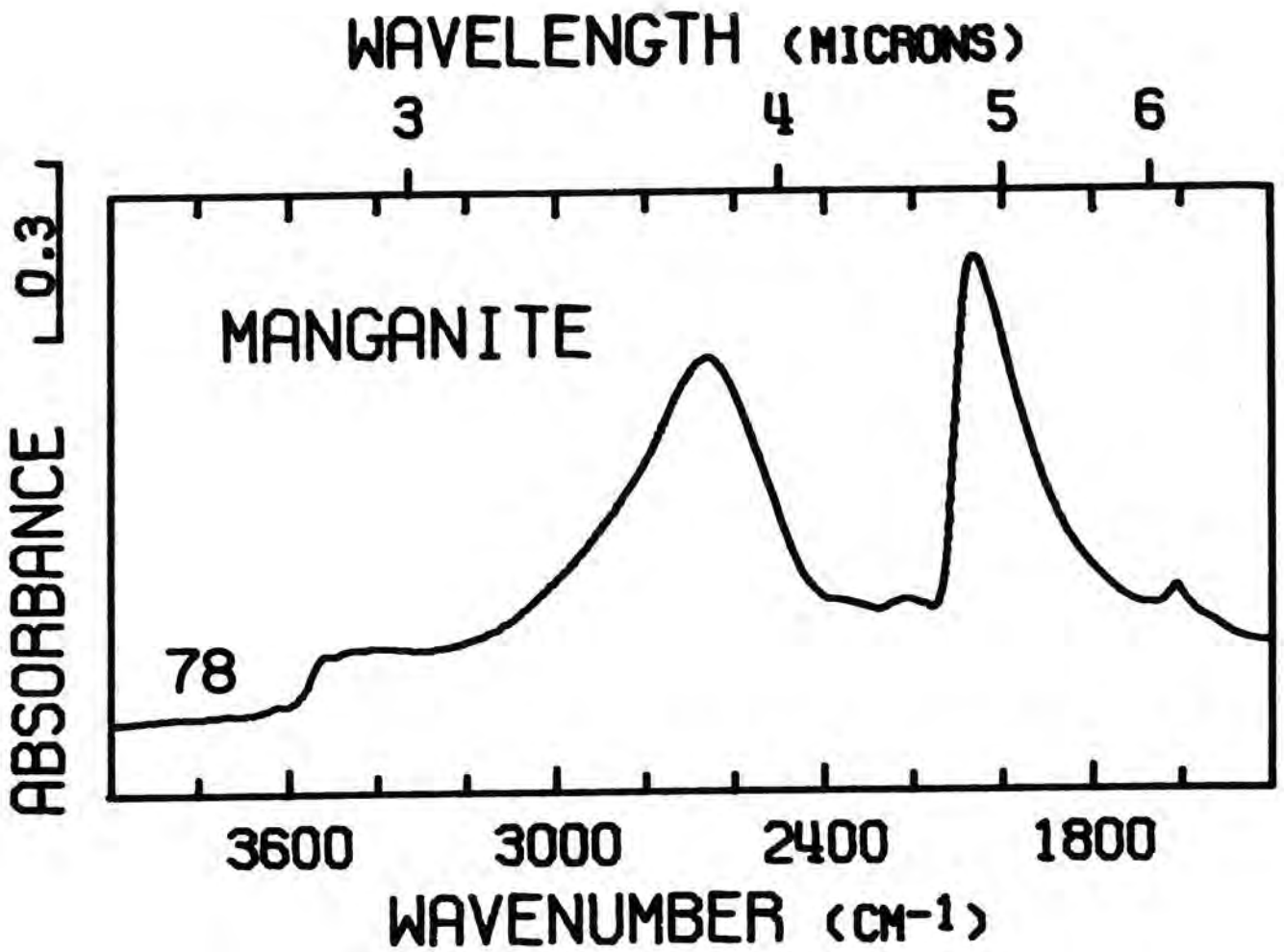


Figure 4A. Infrared spectrum of manganite. Presentation intensity: 81%. Figure continued on following page.



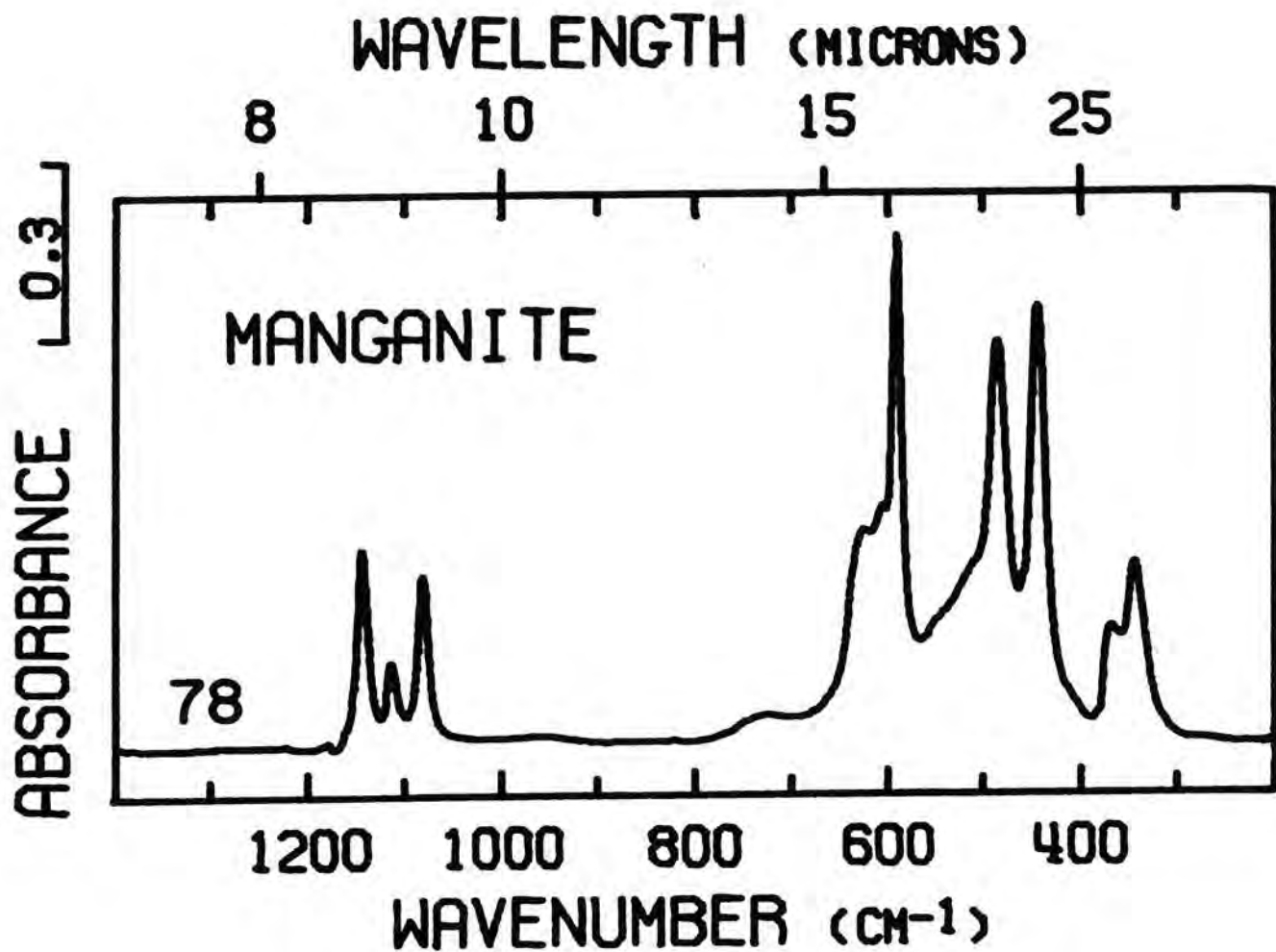


Figure 4A. Continued from preceding page.

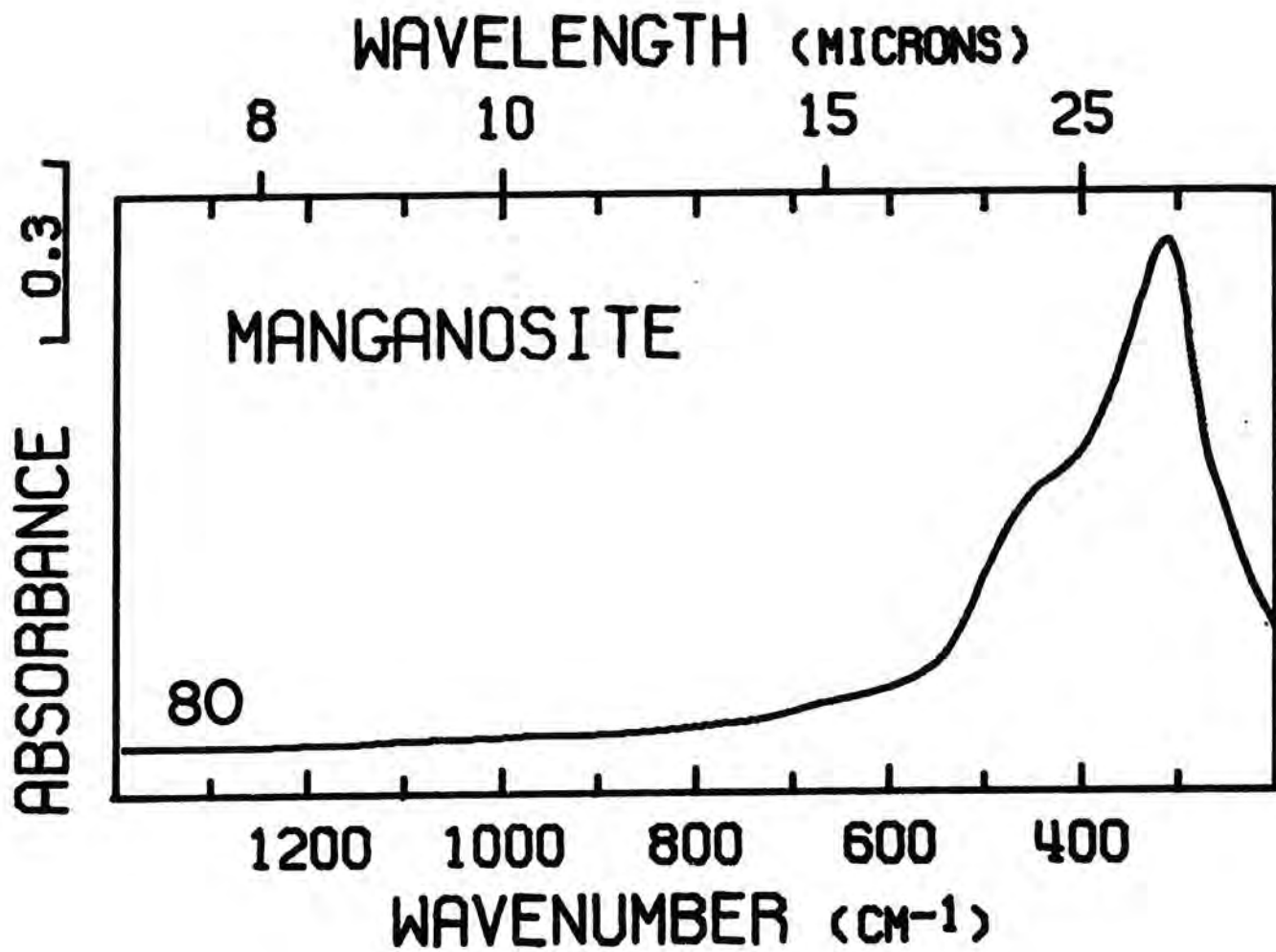


Figure 5A. Infrared spectrum of manganosite. Presentation intensity: 244%.

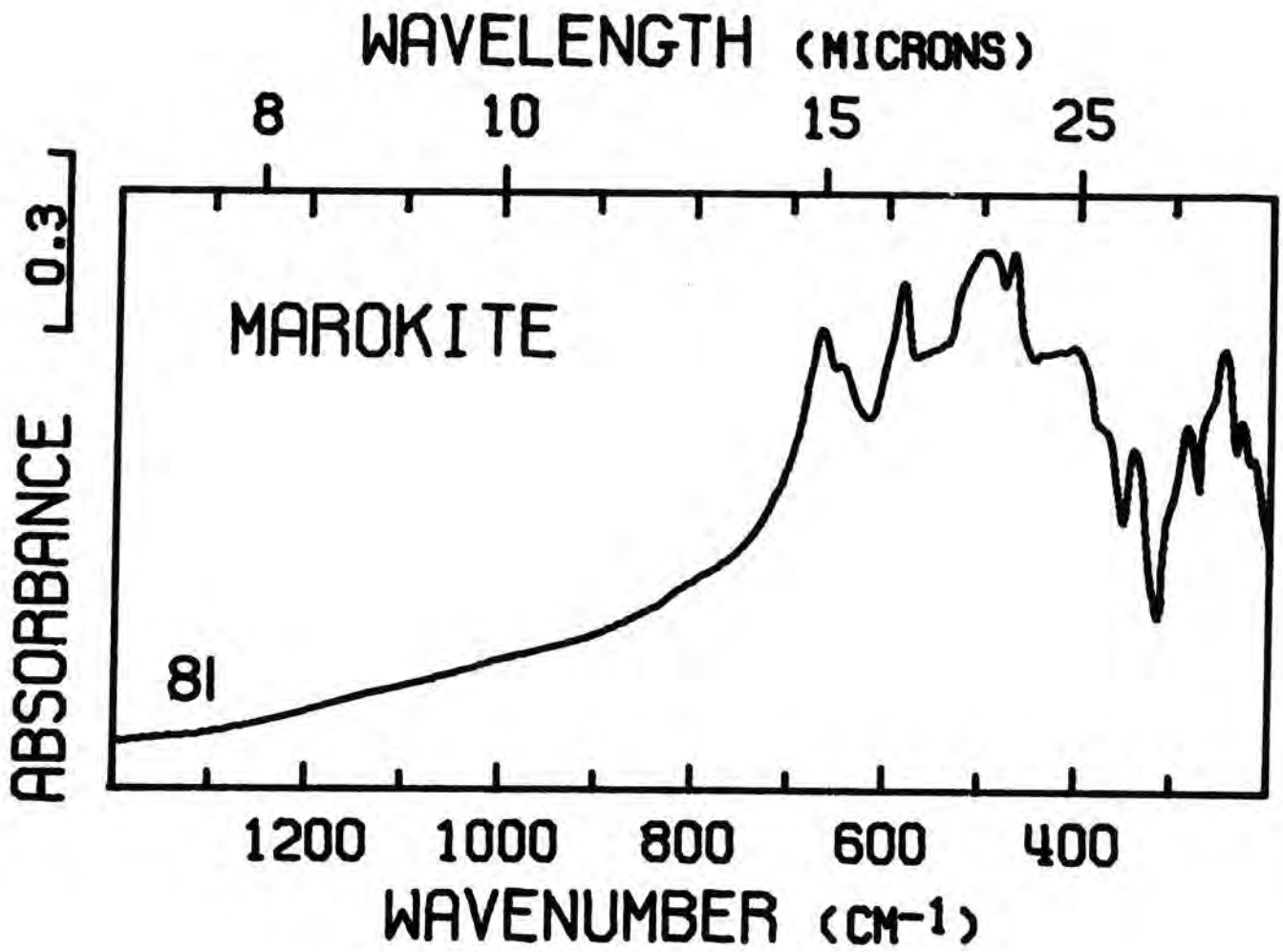


Figure 6A. Infrared spectrum of marokite. Presentation intensity: 414%.

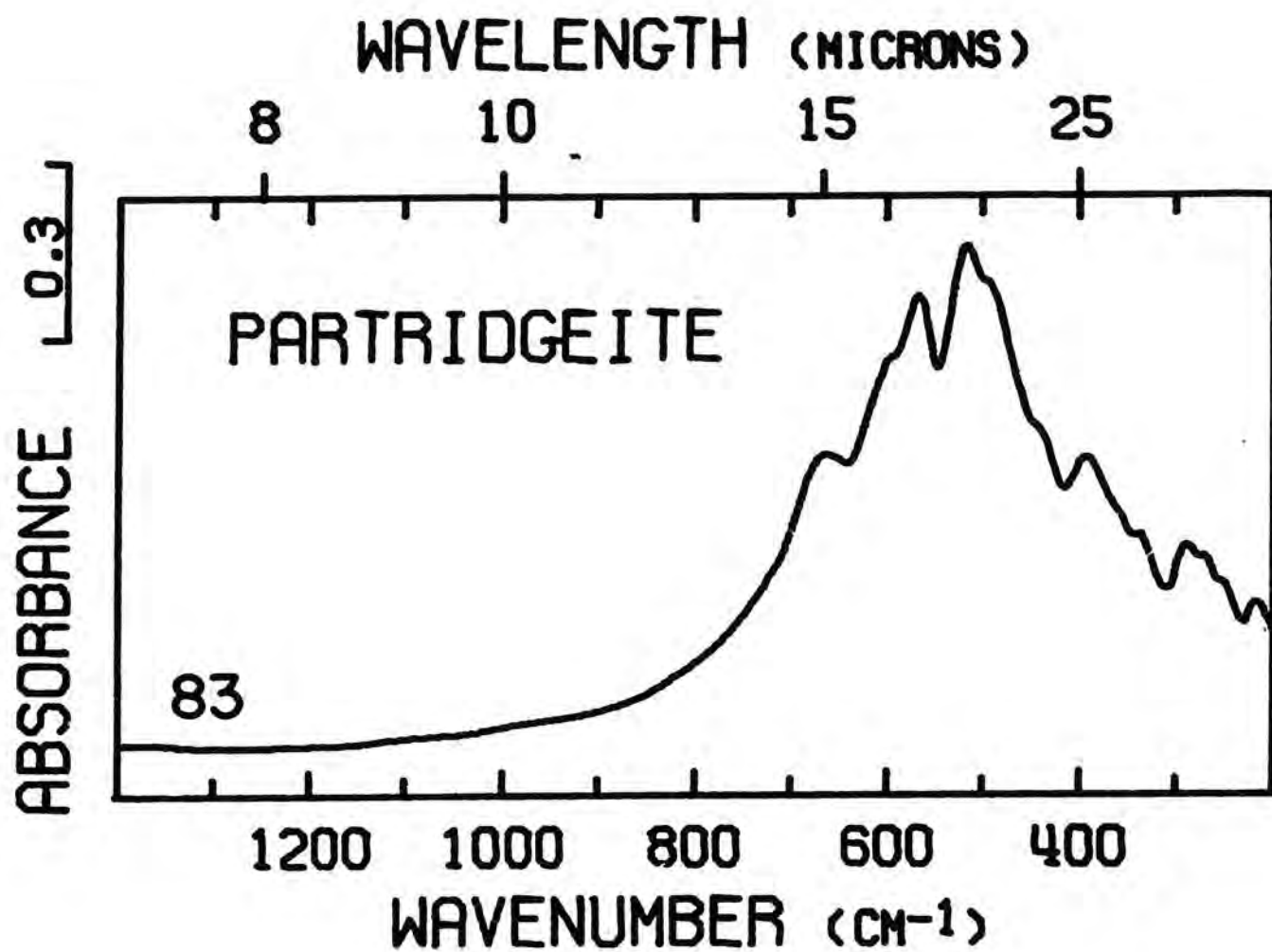


Figure 7A. Infrared spectrum of partridgeite. Presentation intensity: 248%.

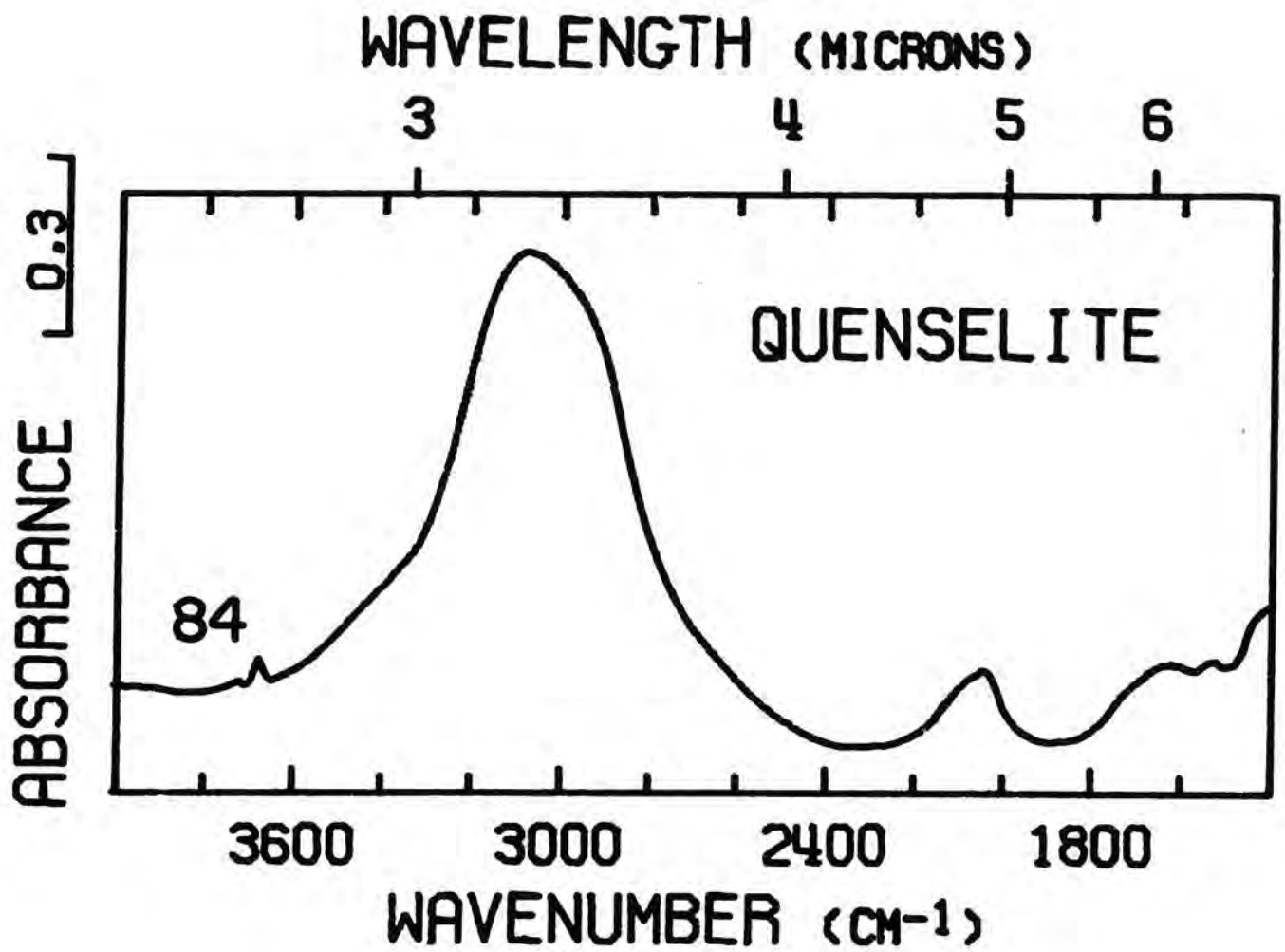


Figure 8A. Infrared spectrum of quenselite. Presentation intensity: 404%. Figure continued on following page.

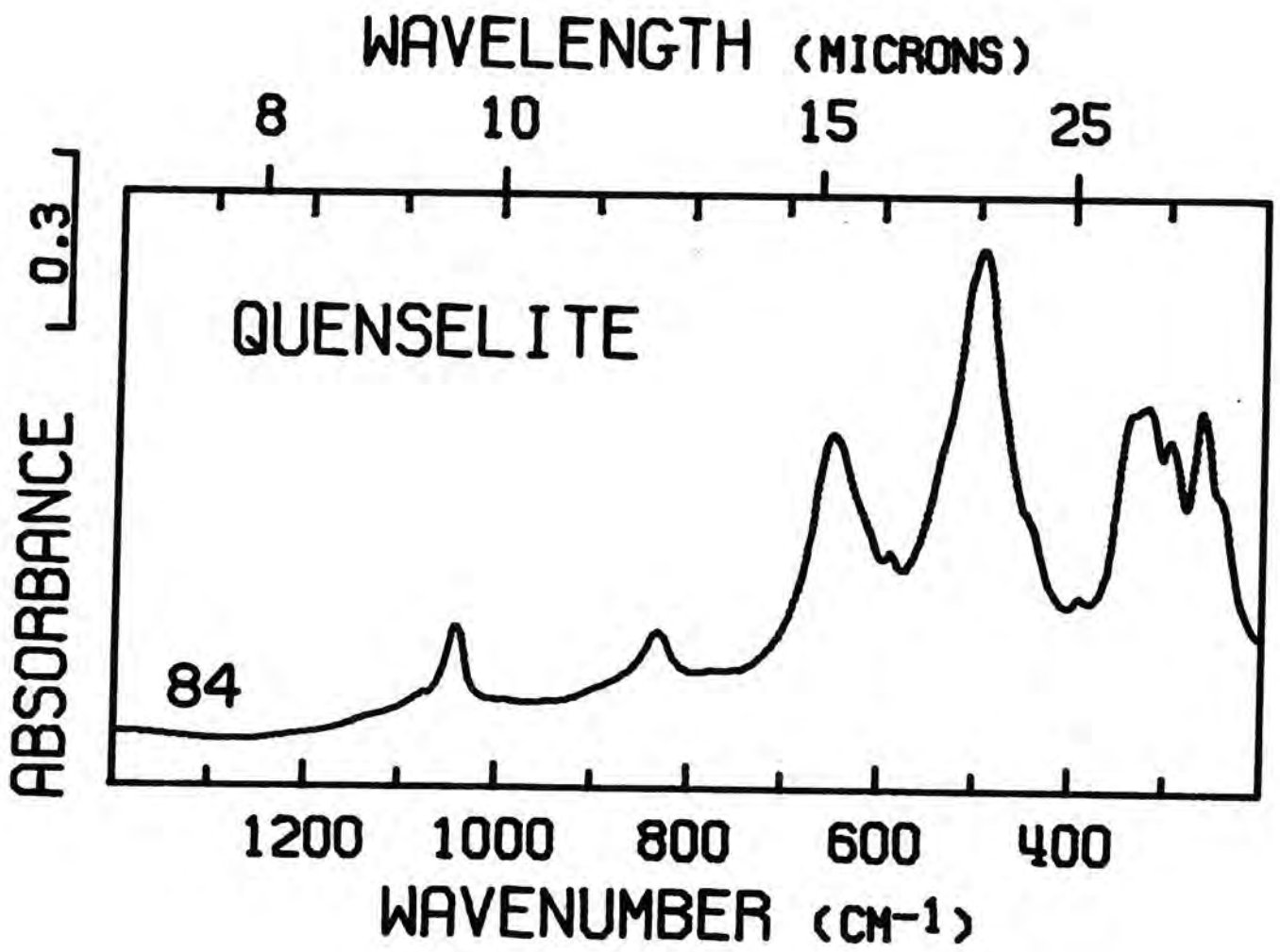


Figure 8A. Continued from preceding page.

## APPENDIX B

The appendix contains infrared spectra of samples listed in Table 1 and Table 1A, which are not contained elsewhere in the paper. Some are included here because they are helpful but not necessary to the discussions in the text; others, because they show significant differences due to the use of KBr rather than TlBr. At least one spectrum of each of the nearly pure samples in Table 1 and Table 1A are also included here to give a fuller picture of the variation present in infrared spectra of the manganese oxides.

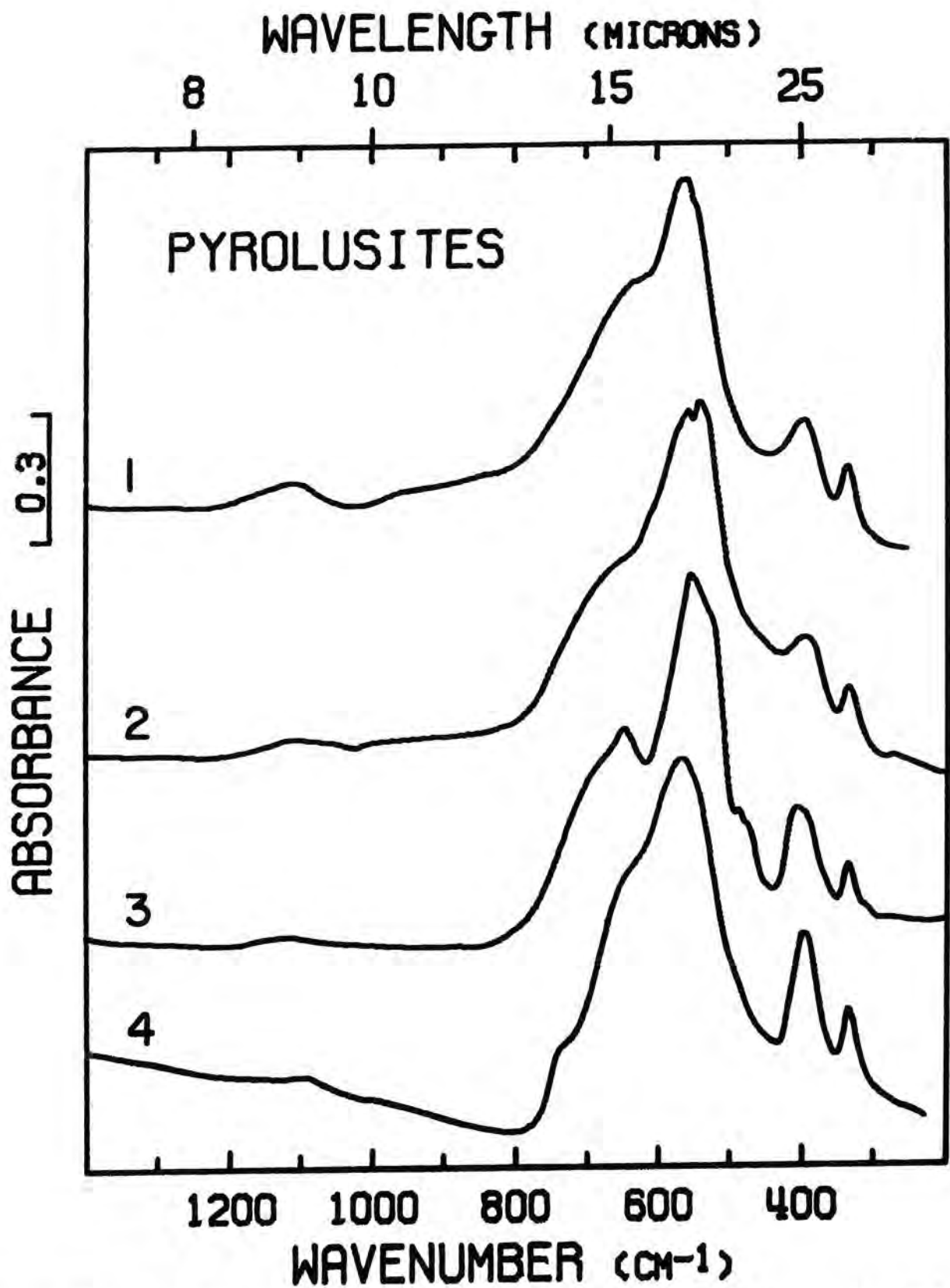


Figure 1B. Infrared spectra of pyrolusites. Presentation intensities and pellet types: #1, 230%, T1Br; #2, 223%, T1Br; #3, 142%, T1Br; #4, 148%, KBr.



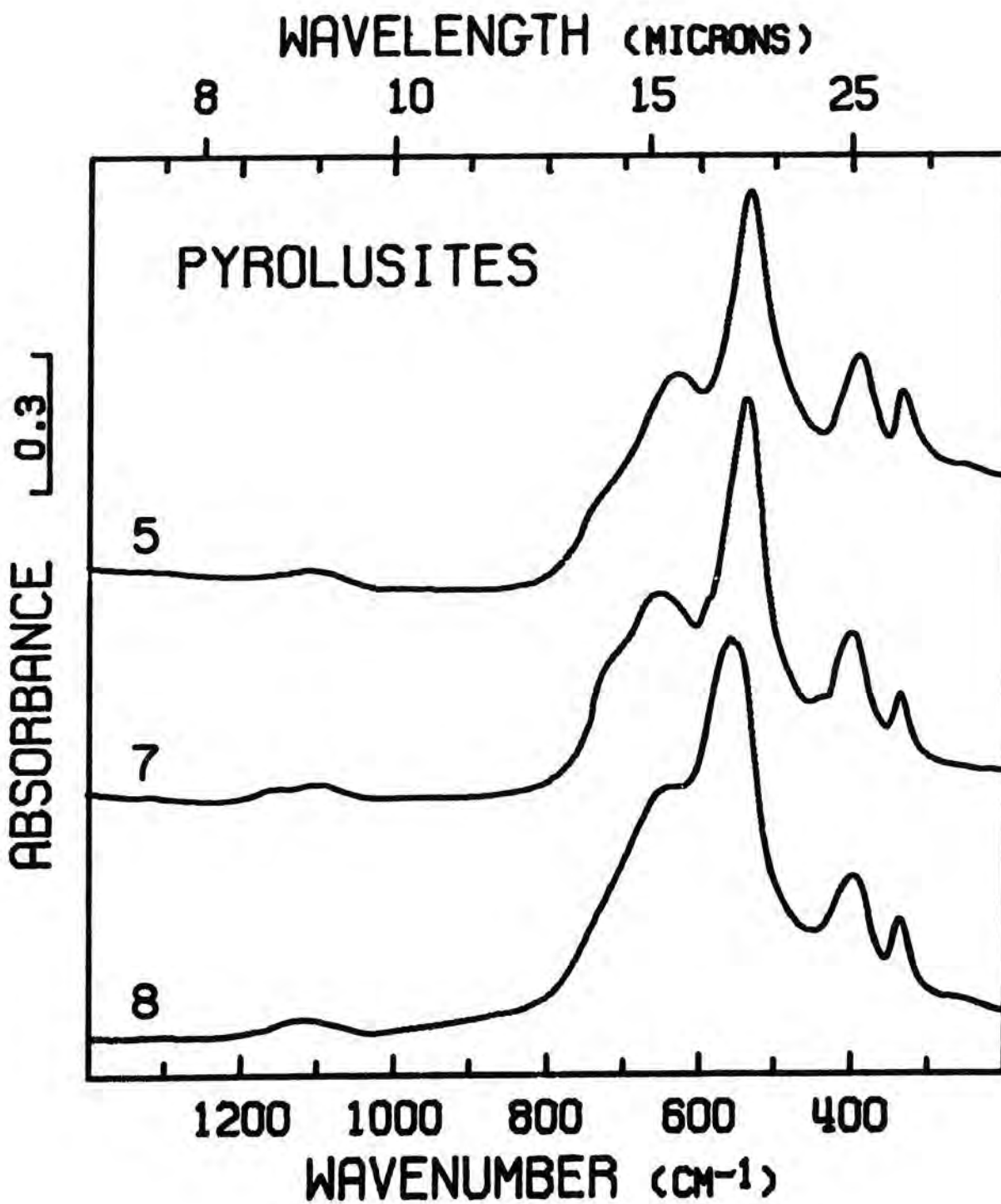


Figure 2B. Infrared spectra of pyrolusites, continued. Presentation intensities and pellet types: #5, 264%, T1Br; #7, 101%, T1Br; #8, 177%, T1Br.

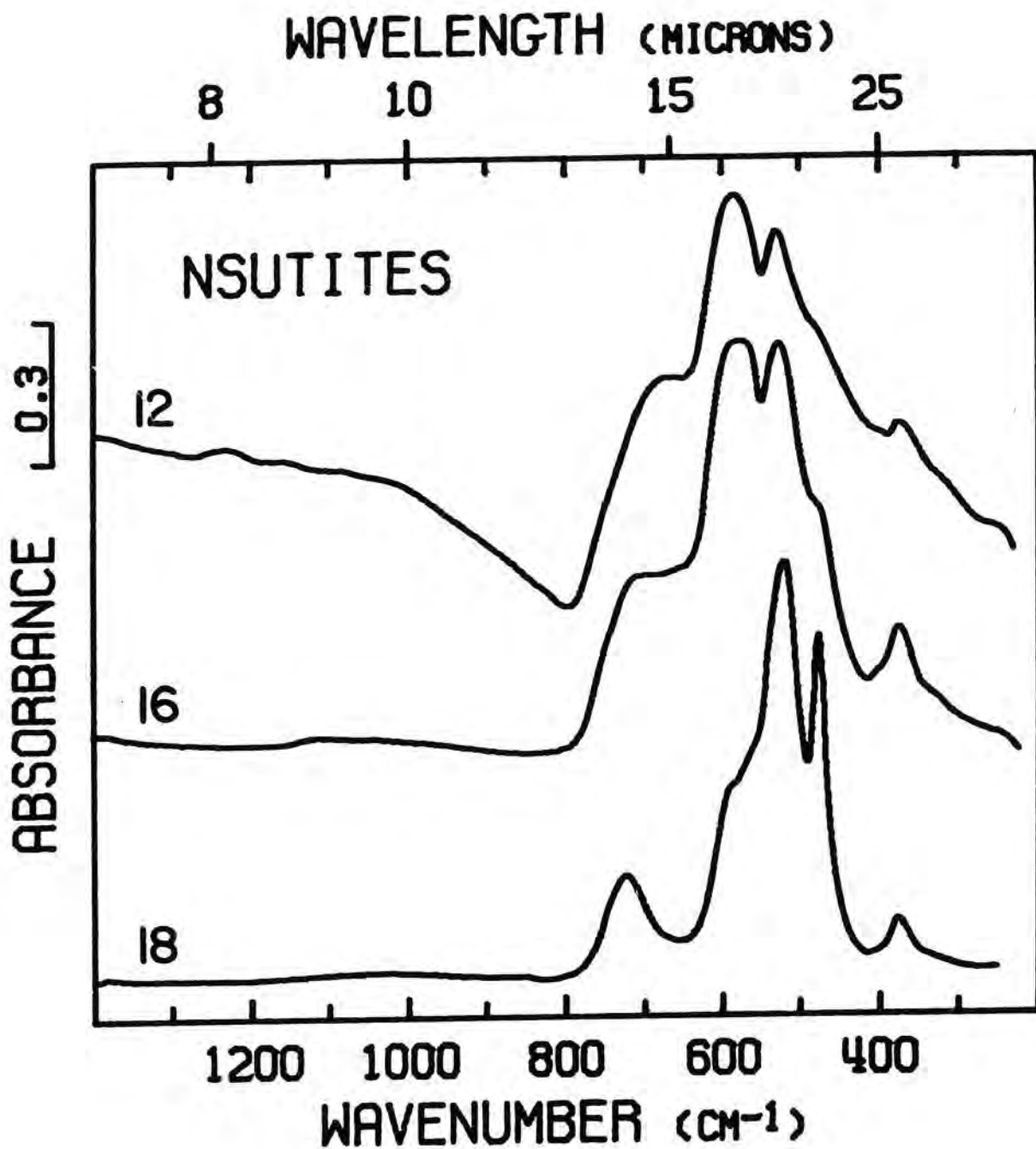


Figure 3B. Infrared spectra of nsutites. Presentation intensities and pellet types: #12, 280%, KBr; #16, 147%, KBr; #18, 79%, KBr.

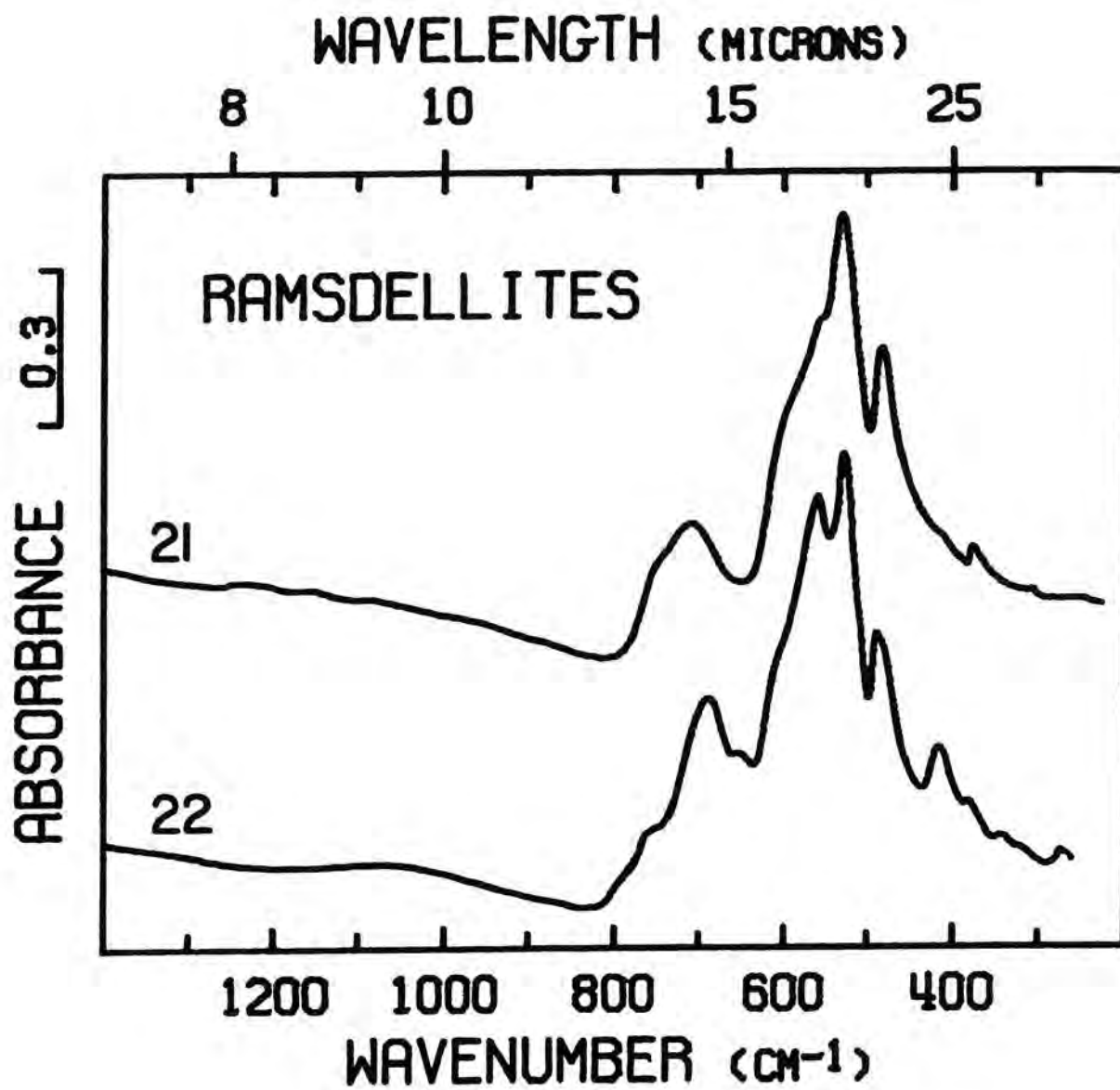


Figure 4B. Infrared spectra of ramsdellites. Presentation intensities and pellet types: #21, 161%, KBr; #22, 161%, KBr.

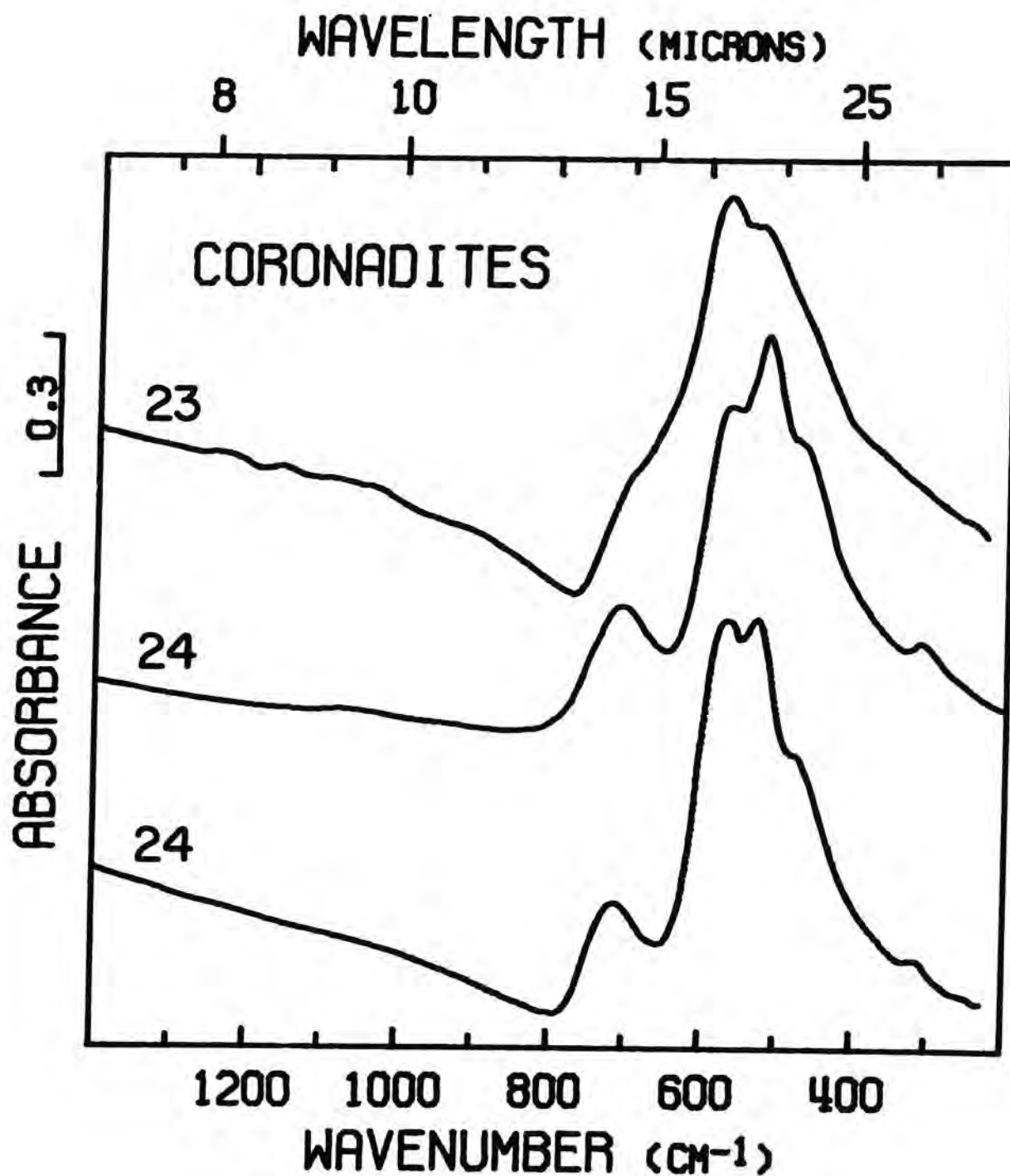


Figure 5B. Infrared spectra of coronadites. Presentation intensities and pellet types: #23, 404%, KBr; #24, 256%, TlBr; #24, 294%, KBr.

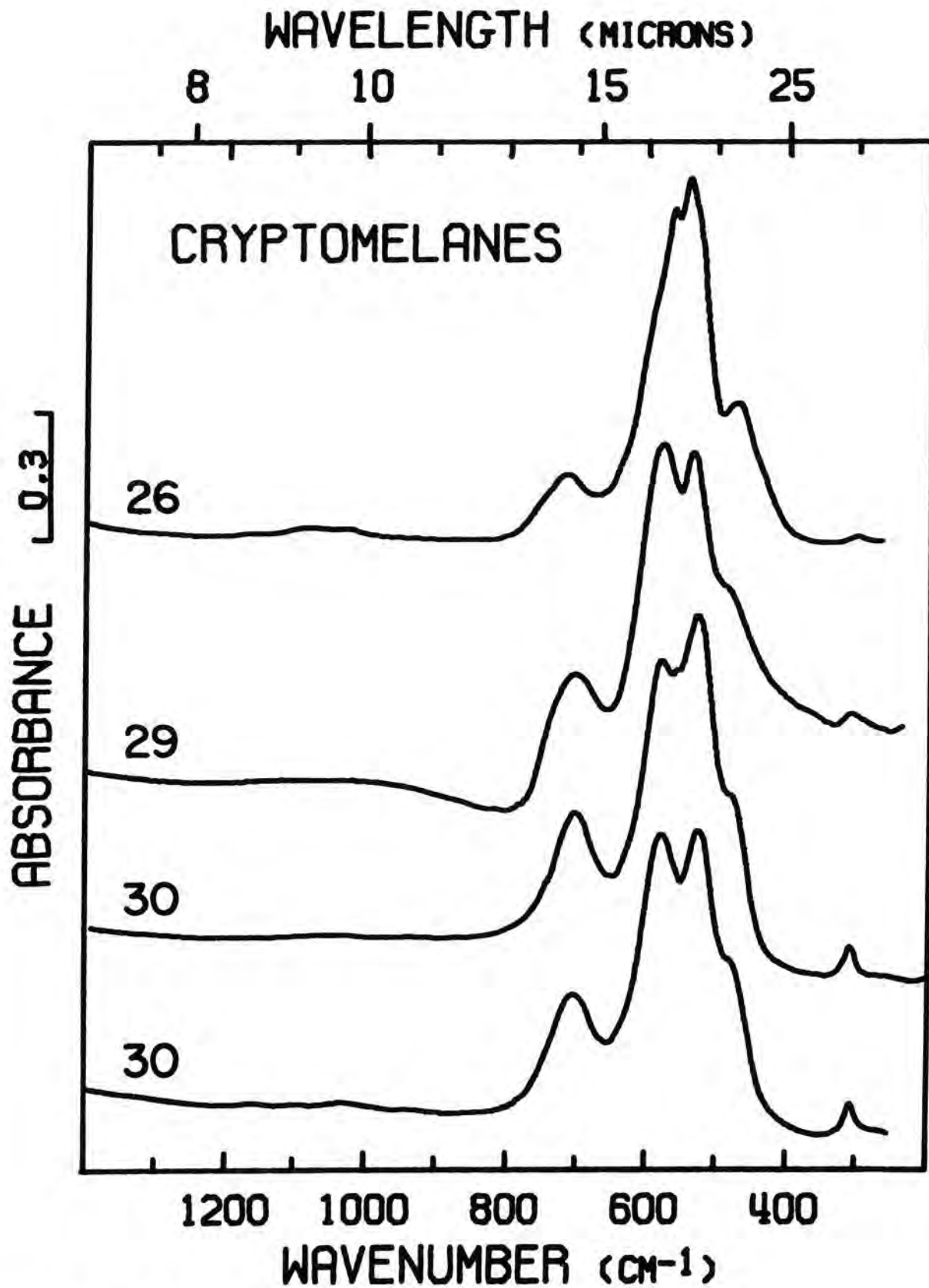


Figure 6B. Infrared spectra of cryptomelanines. Presentation intensities and pellet types: #26, 87%, KBr; #29, 243%, KBr; #30, 124%, TlBr; #30, 183%, KBr.

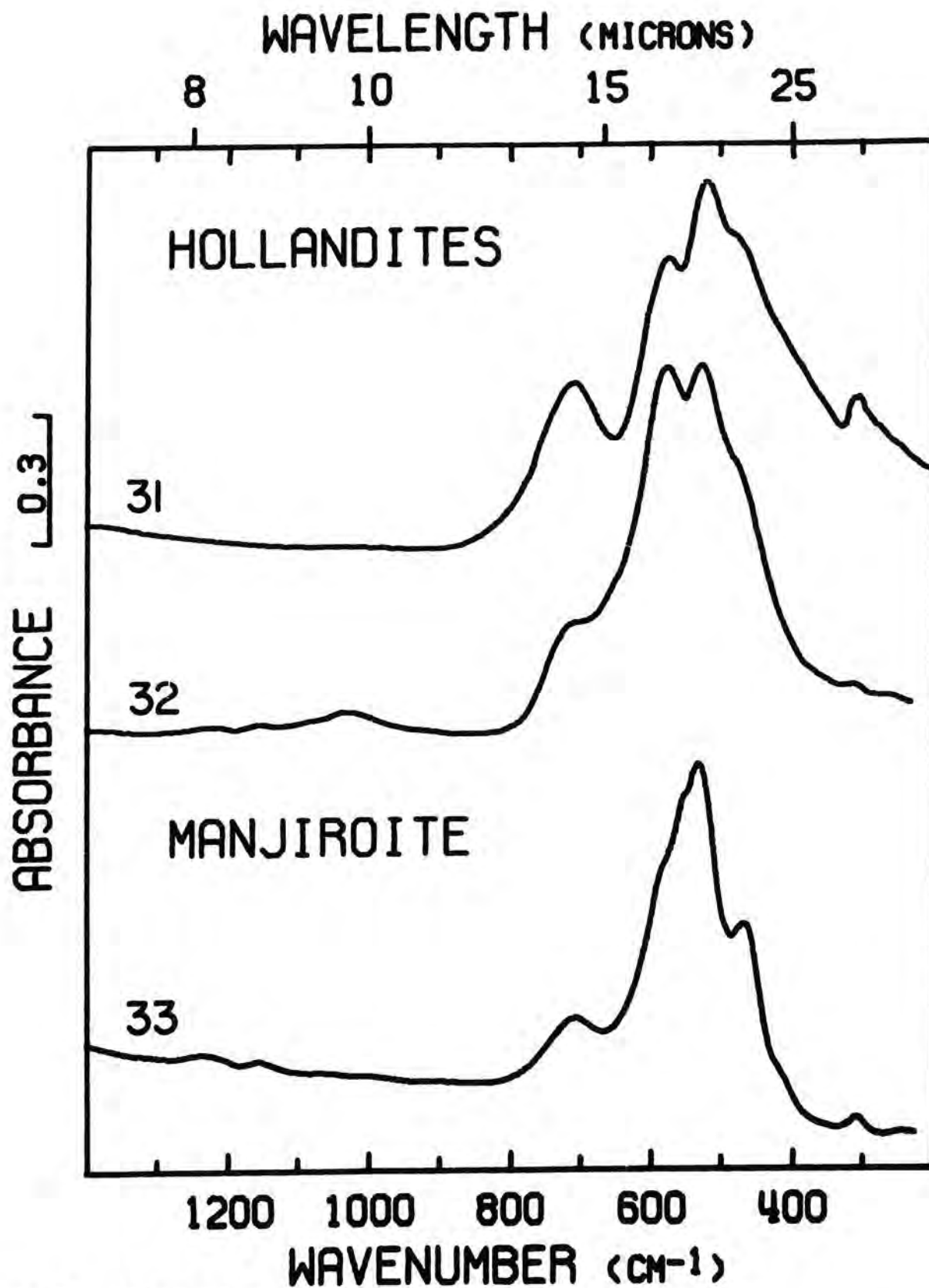


Figure 7B. Infrared spectra of hollandites and manjiroite.  
 Presentation intensities and pellet types: #31, 252%, TlBr; #32,  
 186%, KBr; #33, 118%, KBr.

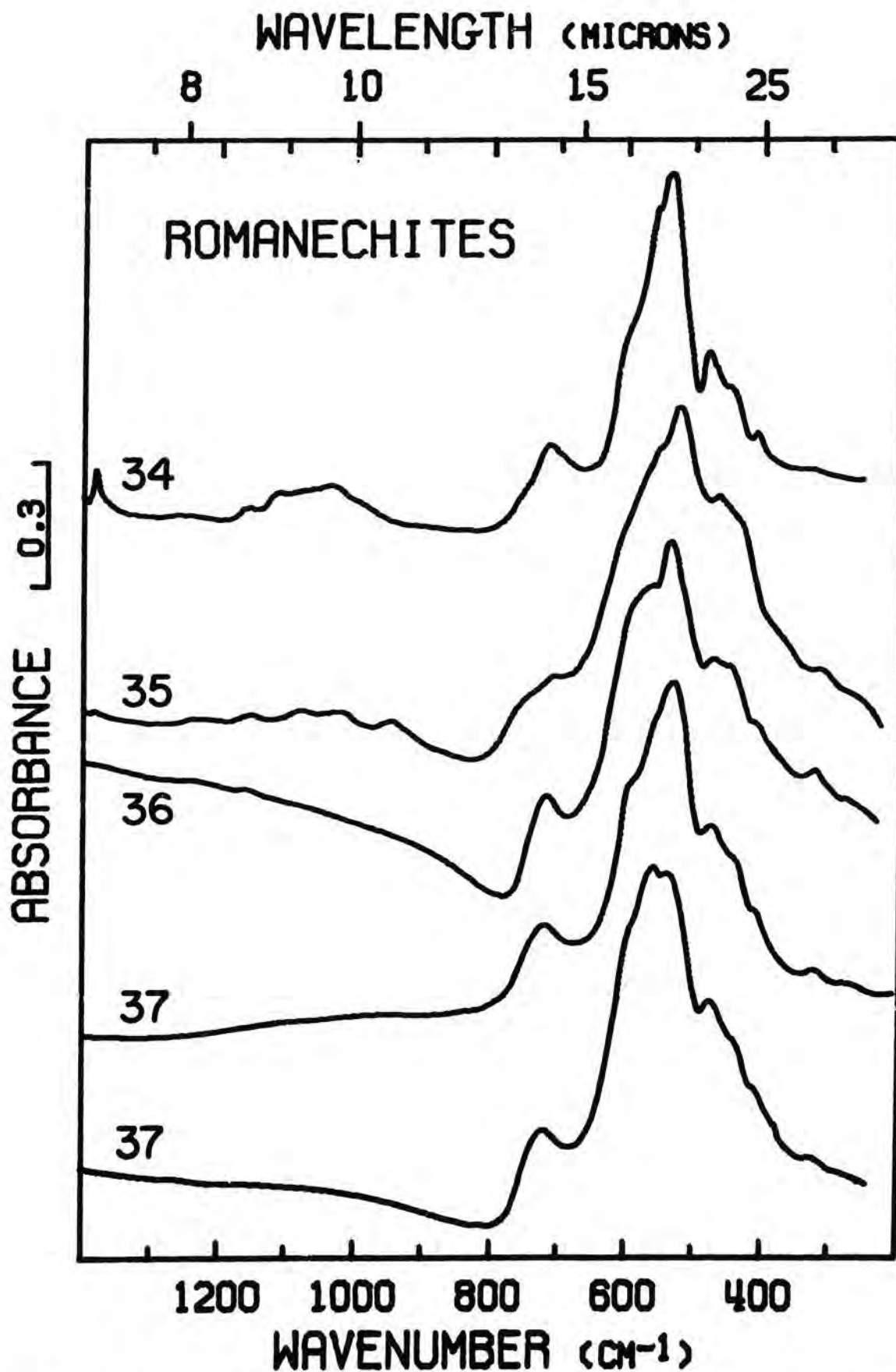


Figure 8B. Infrared spectra of romanechites. Presentation intensities and pellet types: #34, 102%, KBr; #35, 207%, KBr; #36, 280%, KBr; #37, 138%, TlBr; #37, 180%, KBr.

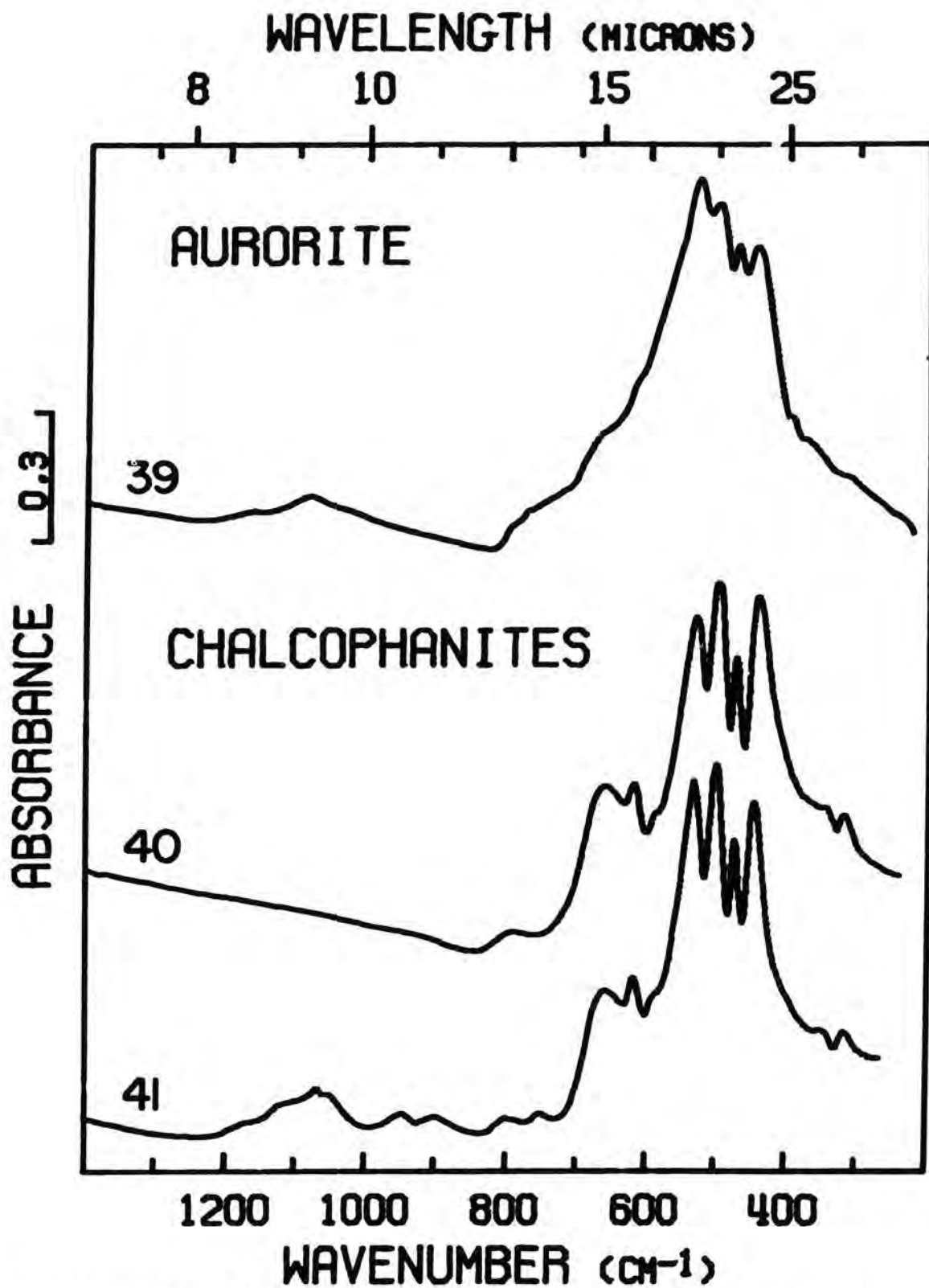


Figure 9B. Infrared spectra of aurorite and chalcophanites.  
 Presentation intensities and pellet types: #39, 256%, KBr; #40, 164%, KBr; #41, uncertain, KBr.



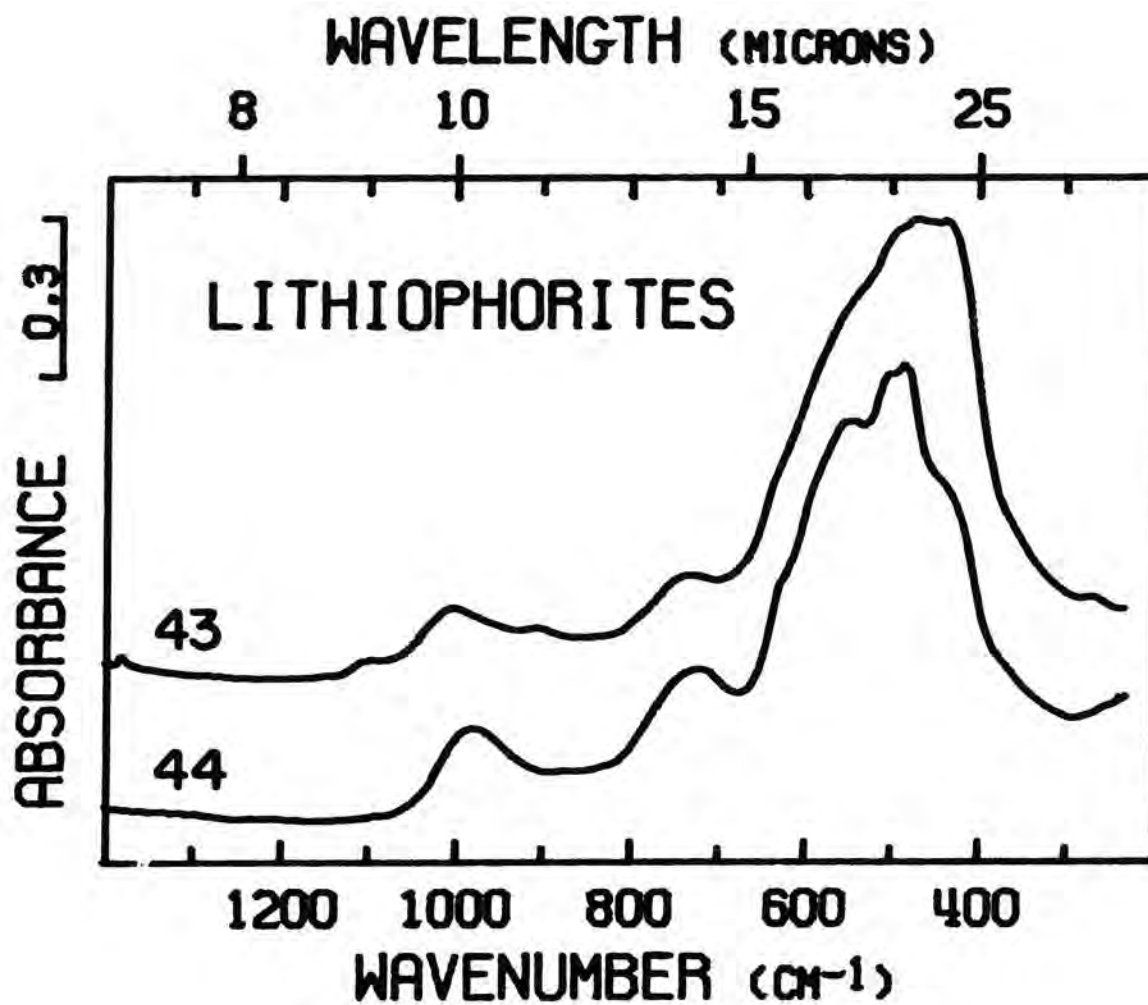


Figure 10B. Infrared spectra of lithiophorites. Presentation intensities and pellet types: #43, 151%, KBr; #44, 167%, KBr.

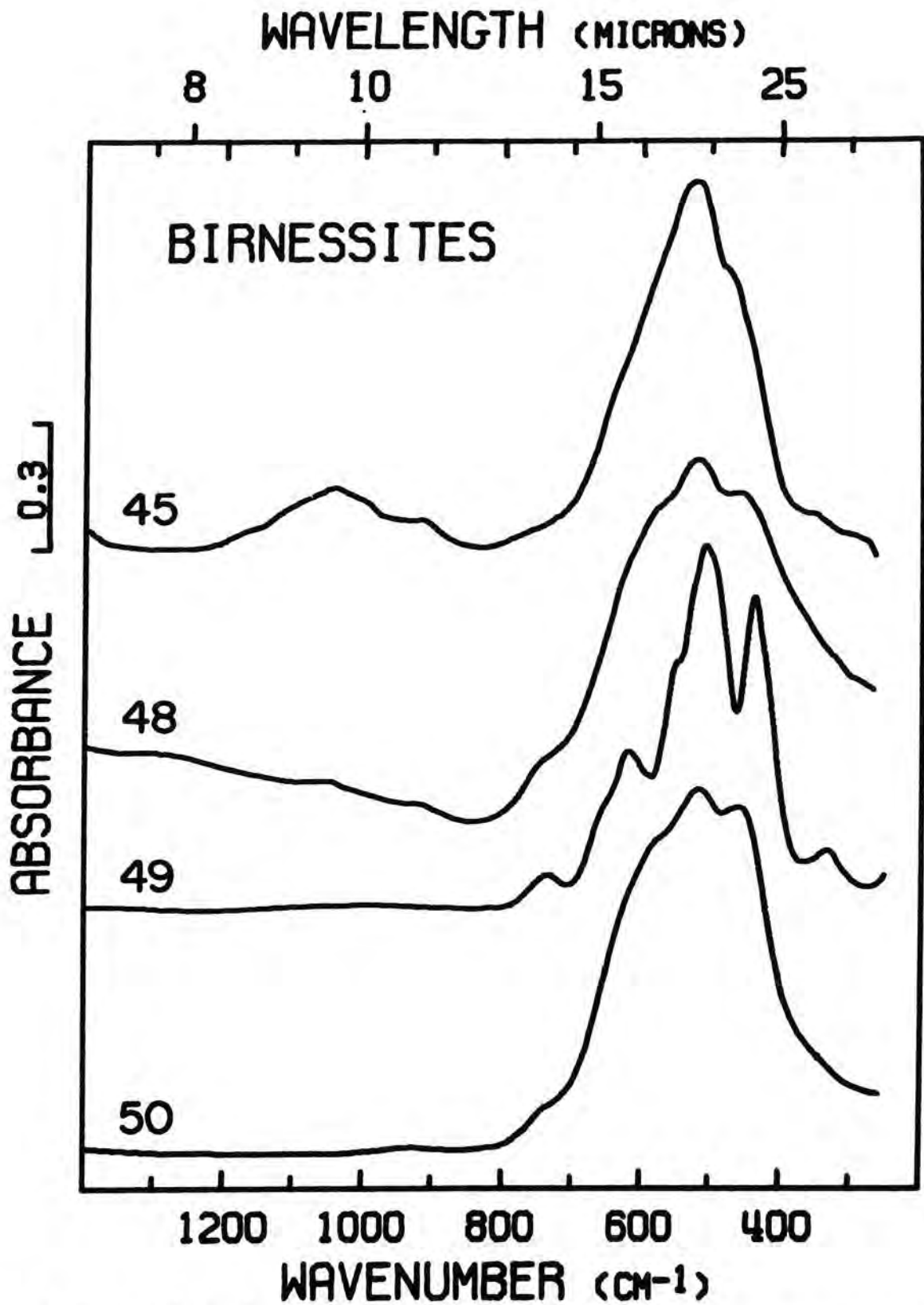


Figure 11B. Infrared spectra of birnessites. Presentation intensities and pellet types: #45, uncertain, KBr; #48, 350%, KBr; #49, 101%, KBr; #50, 163%, KBr.

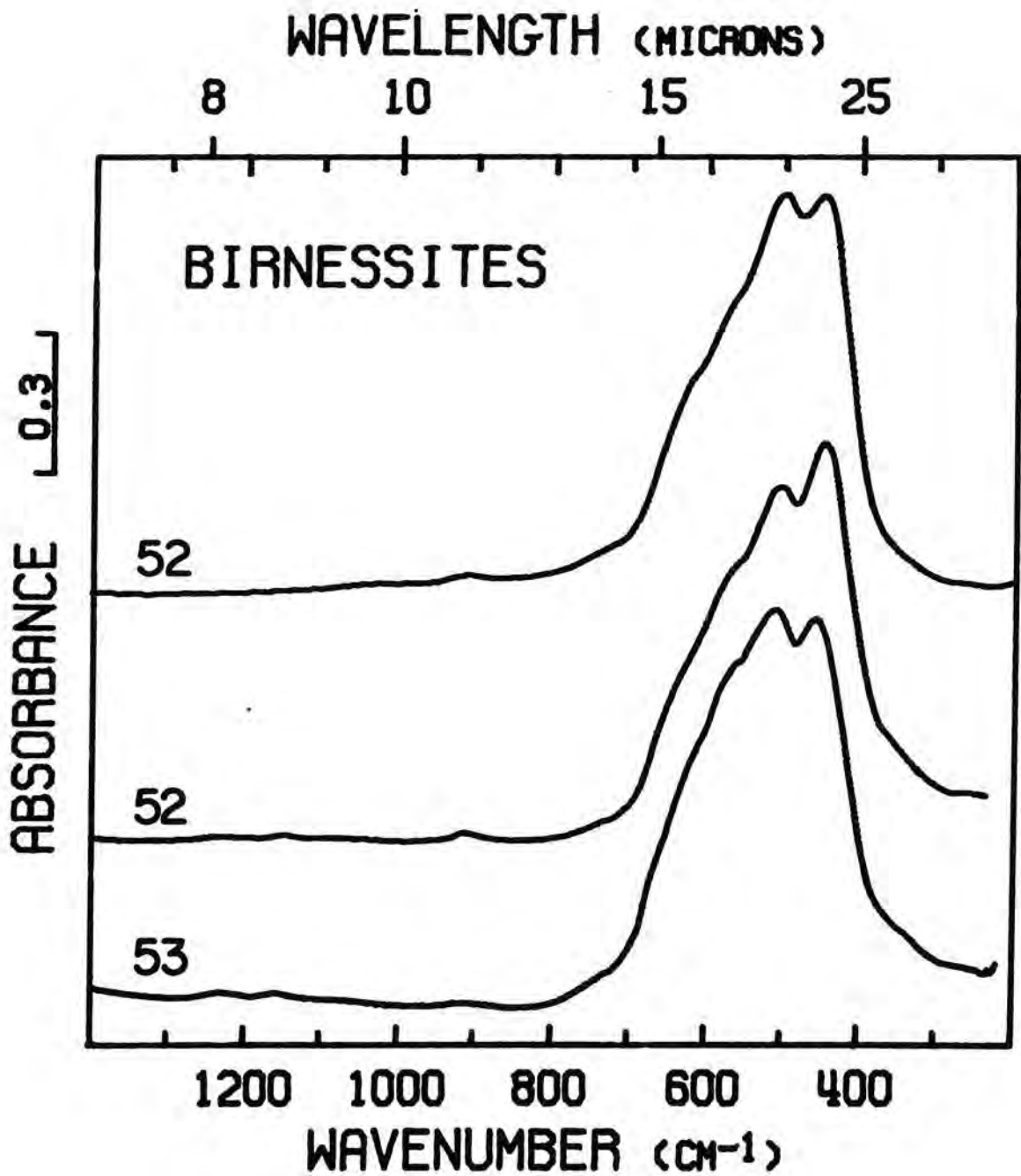


Figure 12B. Infrared spectra of birnessites, continued. Presentation intensities and pellet types: #52, 114%, T1Br; #52, 114%, KBr; #53, 140%, KBr.

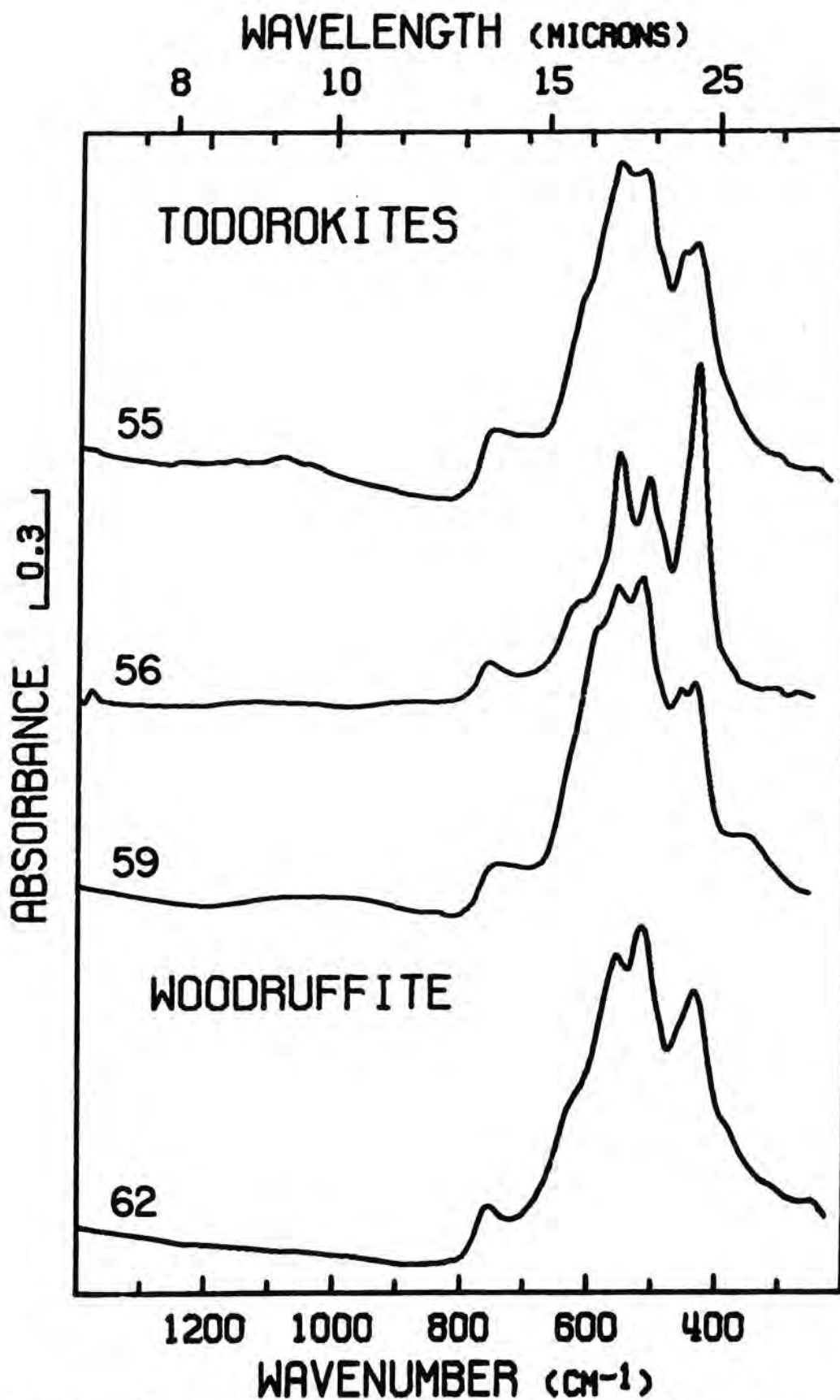


Figure 13B. Infrared spectra of todorokites and woodruffite. Presentation intensities and pellet types: #55, 155%, KBr; #56, 198%, KBr; #59, 172%, KBr; #62, 175%, KBr.

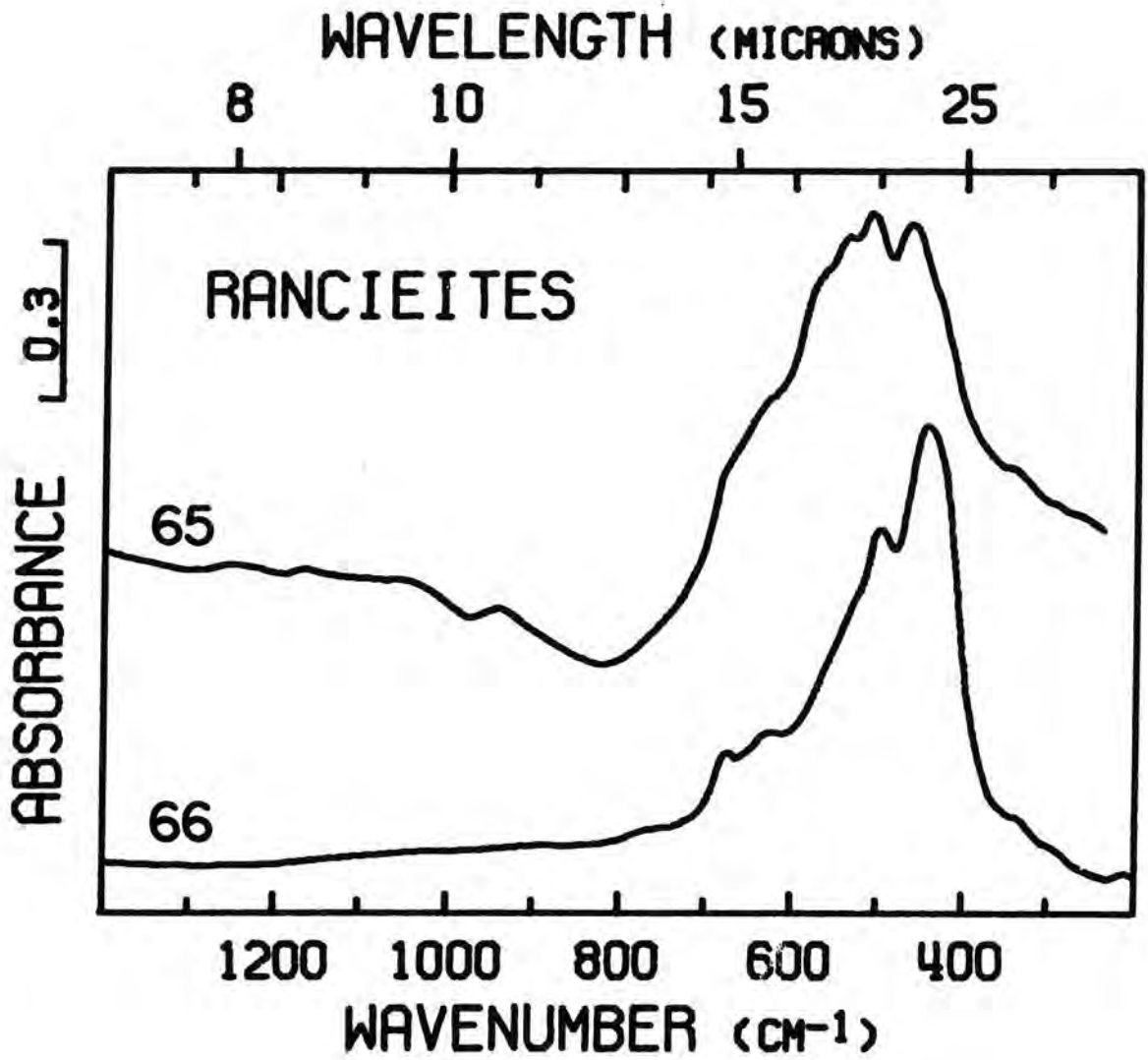


Figure 14B. Infrared spectra of rancieites. Presentation intensities and pellet types: #65, 412%, KBr; #66, 112%, TlBr. Absorption of braunite impurity removed from the spectrum of #65 (see text footnote 3).

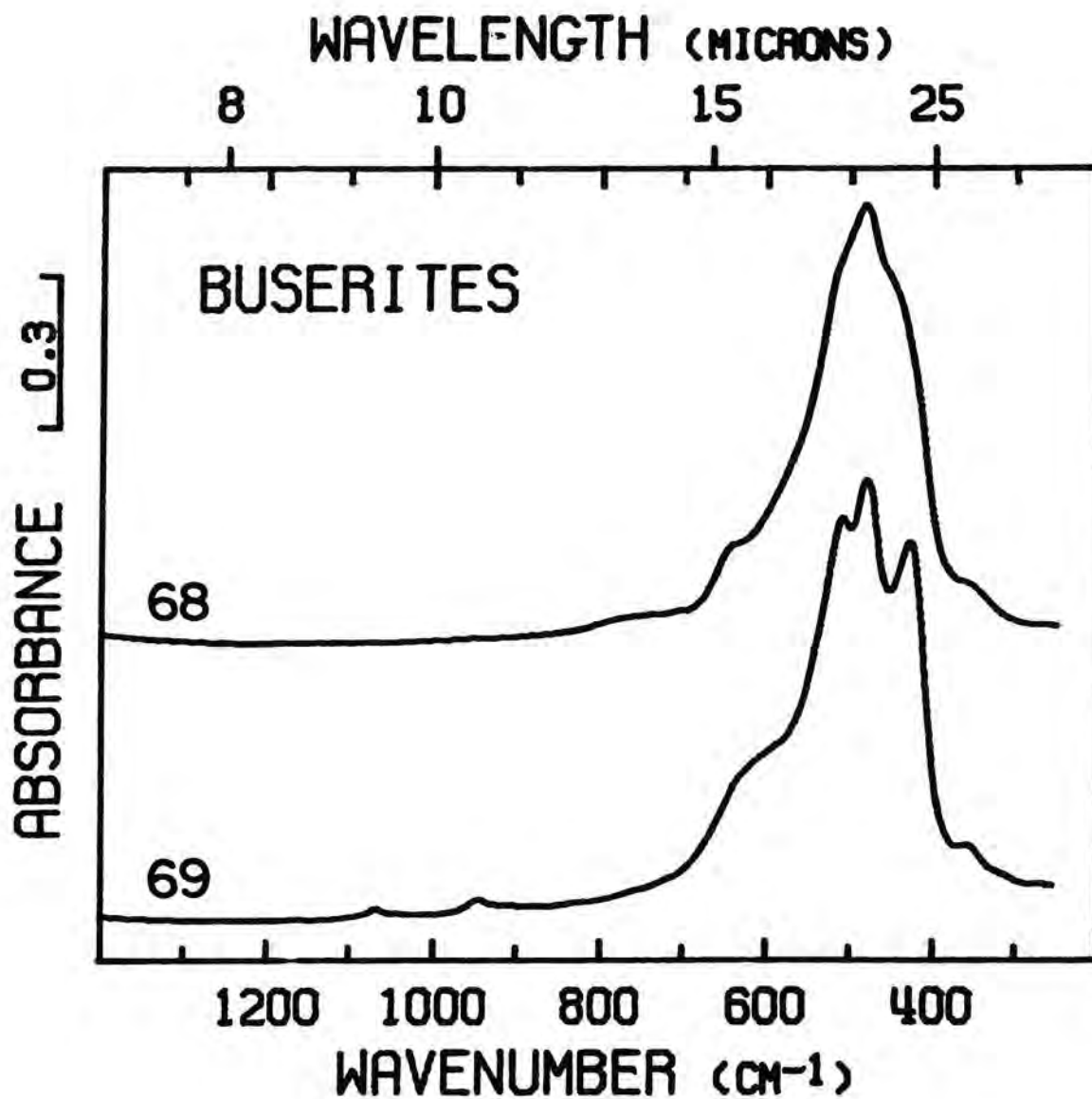


Figure 15B. Infrared spectra of buserites. Presentation intensities and pellet types: #68, 120%, KBr; #69, 97%, KBr.

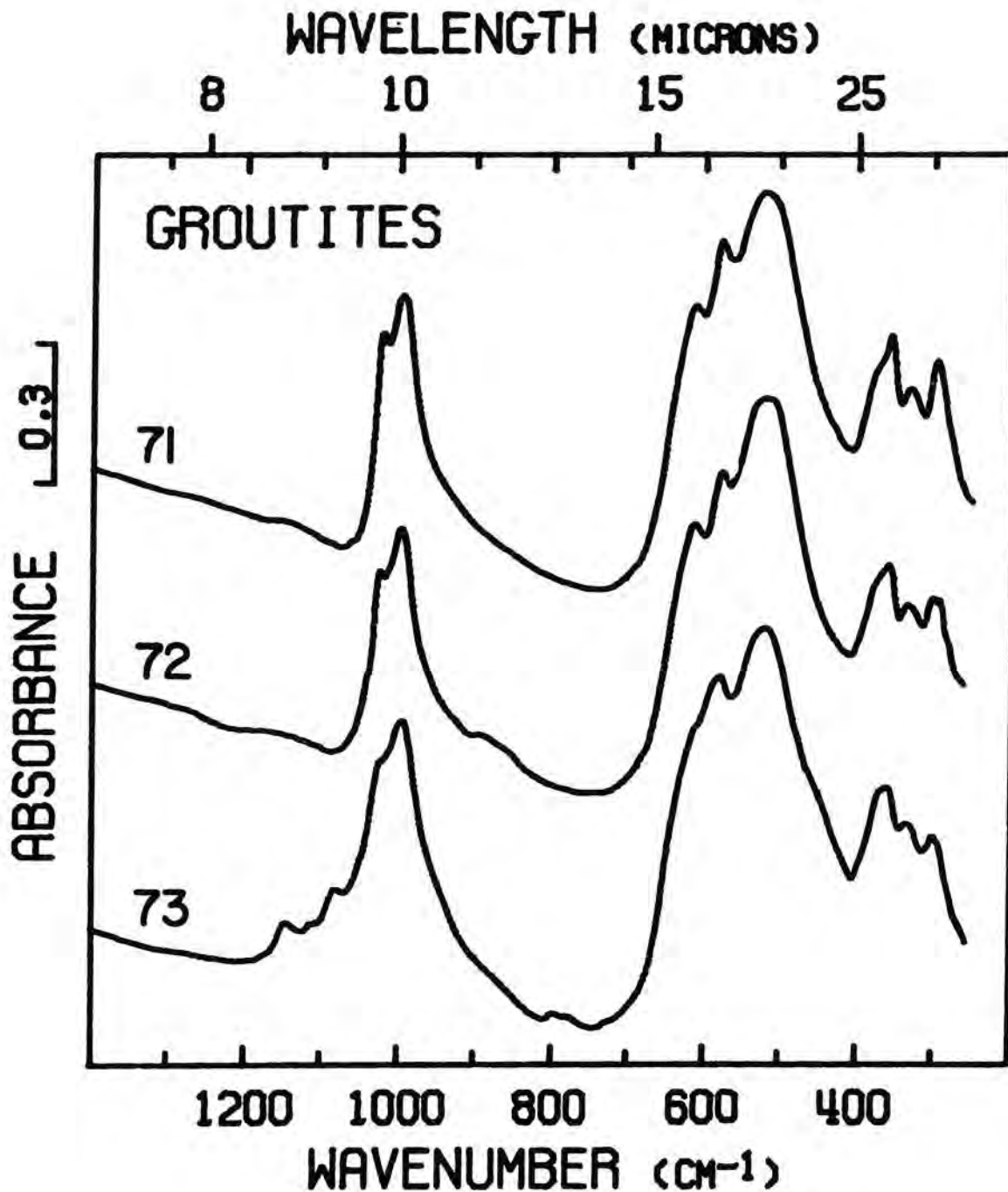


Figure 16B. Infrared spectra of groutites. Presentation intensities and pellet types: #71, 244%, KBr; #72, 256%, KBr; #73, 296%, KBr.

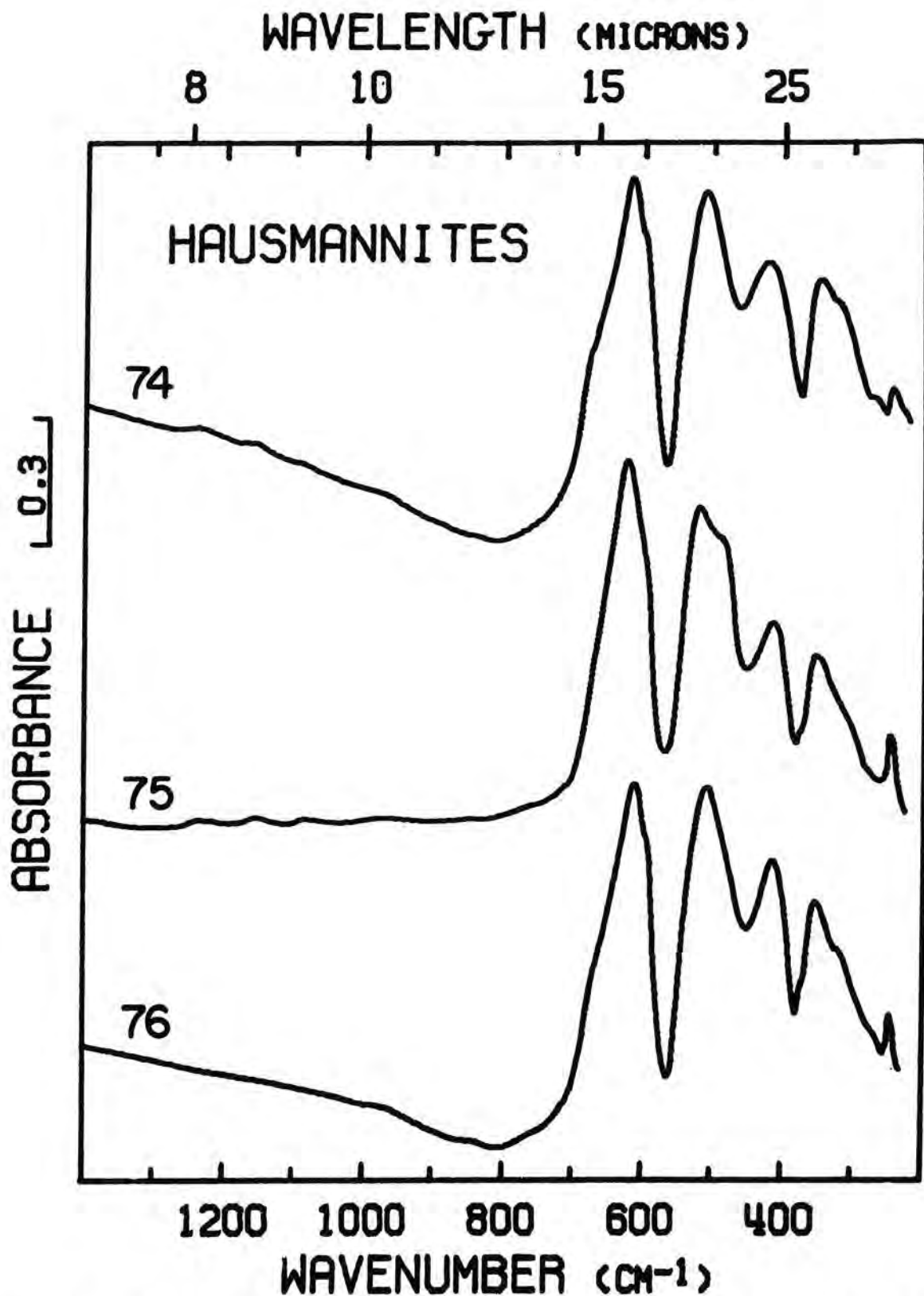


Figure 17B. Infrared spectra of hausmannites. Presentation intensities and pellet types: #74, 316%, KBr; #75, 188%, KBr; #76, 276%, KBr.



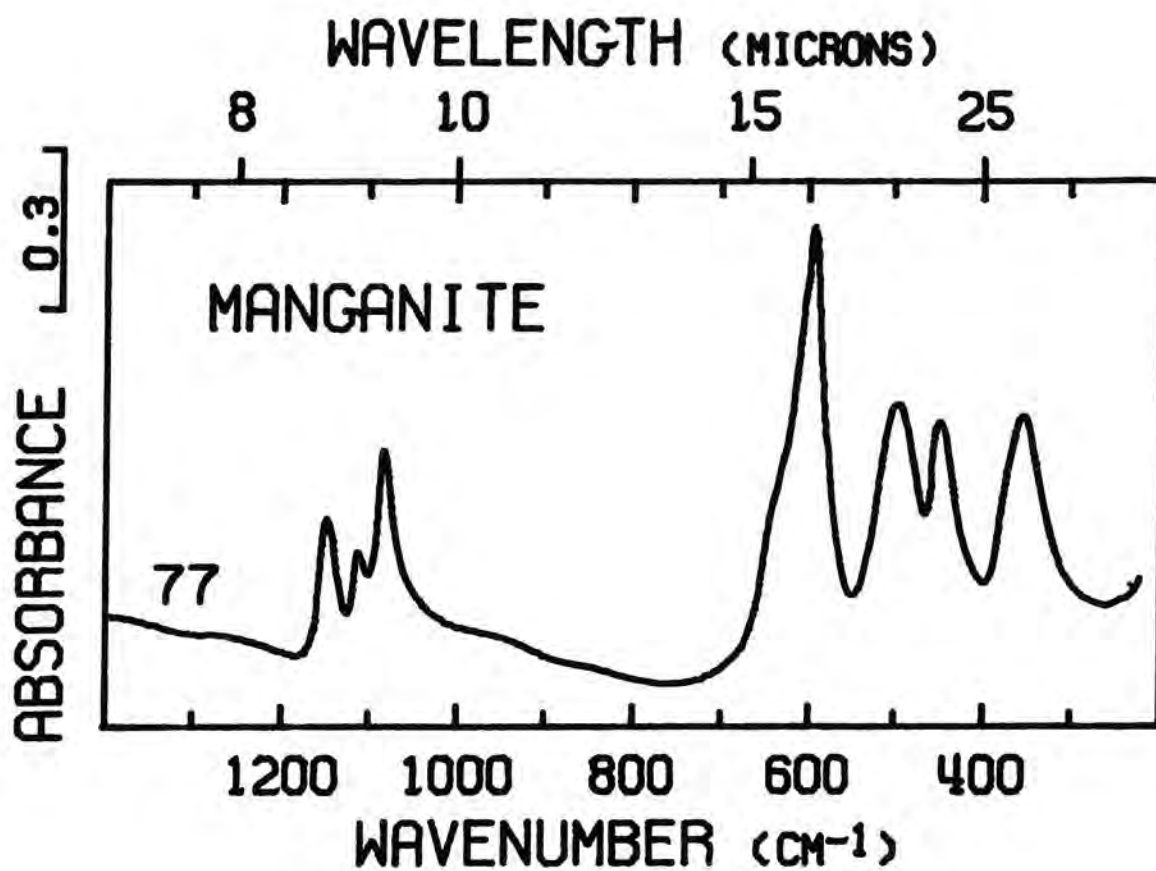


Figure 18B. Infrared spectrum of manganite. Presentation intensity and pellet type: 149%, KBr.

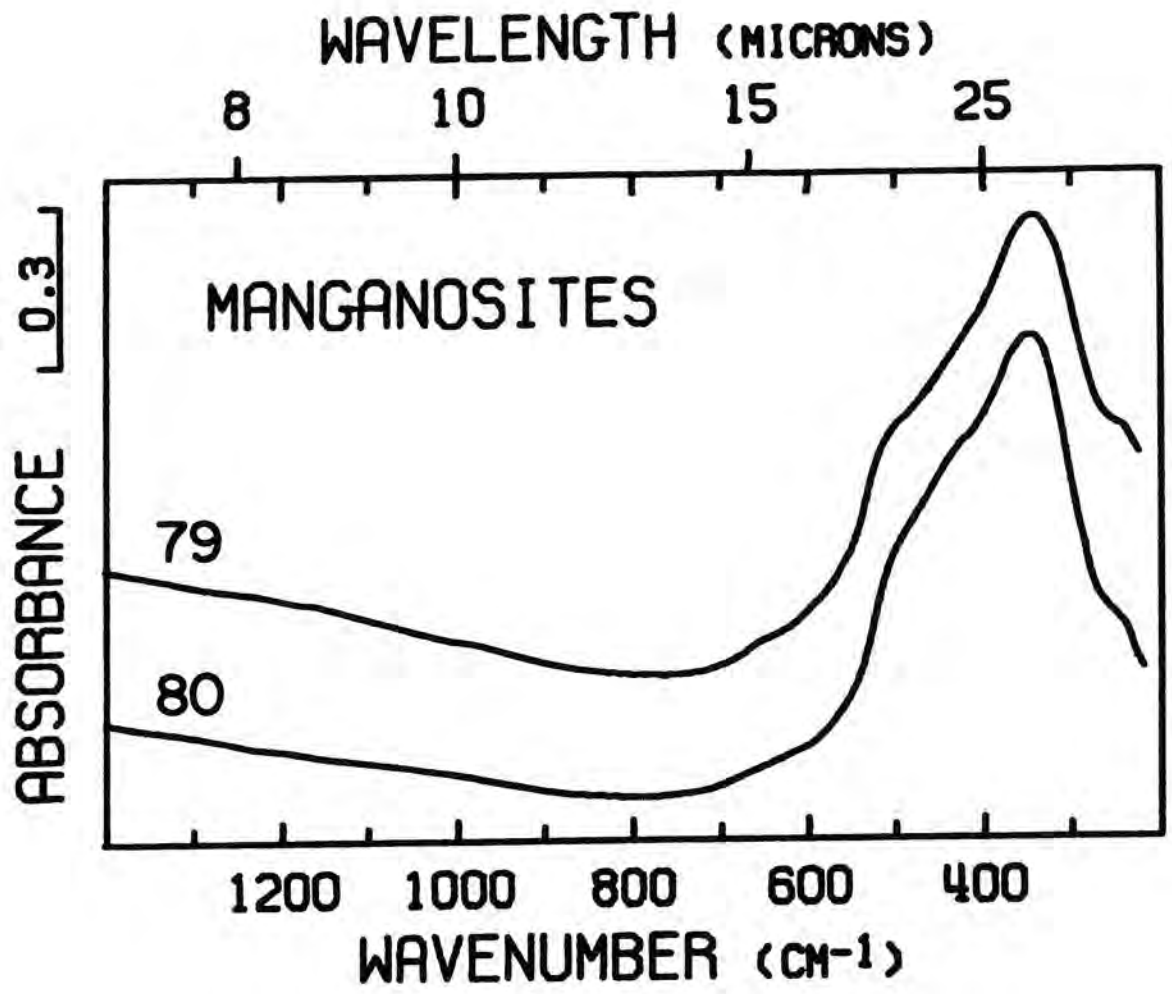


Figure 19B. Infrared spectra of manganosites. Presentation intensities and pellet types: #79, 260%, KBr; #80, 242%, KBr.

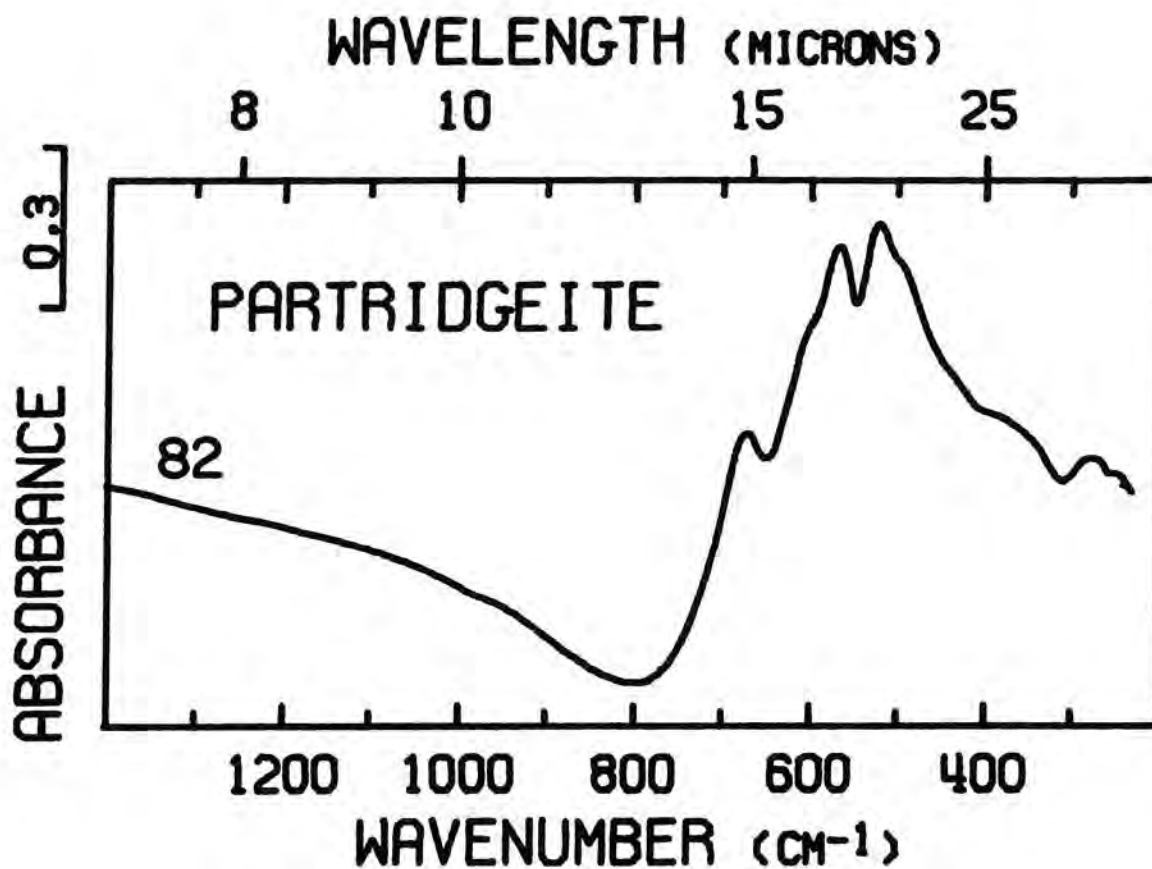


Figure 20B. Infrared spectrum of partridgeite. Presentation intensity and pellet type: 294%, KBr.