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INFRARED STUDY OF THE CARBONATE MINERALS

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ABSTRACT

Infrared spectra of 27 common and rare carbonates are described. Each carbonate shows characteristic absorption bands, some of which differ more or less from published curves. Among the isomorphous members of the calcite, dolomite, and aragonite groups, a noteworthy shift of absorption bands takes place with longer wave lengths corresponding to an increase in cation radius or mass. The spectral difference between the more common groups may be related to crystal structure. The spectral relationships among the minerals of several groups are not well known, due to the complicated composition and crystal structure. Infrared active groups of CO_3, HCO_3, H_2O, OH, and SO_4 dominate the absorption characteristics.

INTRODUCTION

The infrared spectra of anhydrous carbonates among minerals and chemical compounds have been studied to some degree by Schaefer and Schubert (1916), Schaefer et al. (1926), Menzies (1931), Halford (1946), Hunt et al. (1950), Adler et al. (1950), Miller and Wilkins (1952), Keller et al. (1952), and Hunt and Turner (1953). Yet a comprehensive infrared survey of the various carbonate mineral groups using a precision spectrophotometer does not appear to have been made.

In this study it is proposed to furnish systematic data on the infrared spectra of these carbonate minerals, and to infer in general terms the correlation between spectral changes and internal structure. The interpretation is incomplete because of the limited number of samples of satisfactory purity and the partial knowledge of the crystal structure of several carbonates. However, a distinct spectral relationship may be demonstrated among members of isomorphous groups, while both major and minor absorption bands appear to be diagnostic for each mineral.

PROCEDURE

The samples examined were obtained primarily from the mineral collections of Columbia University, supplemented by specimens from the American Museum of Natural History, New York, and the United States National Museum, Washington, D. C. (Table 1). All were checked optically and trona, kutnahorite, gaylussite, schroeckingerite, and andersonite were examined by *x*-ray diffraction (Table 1). Samples containing recognizable impurities were eliminated. Infrared specta were obtained with a Perkin-Elmer Model 21 double beam recording infrared

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TABLE 1. CARBONATE MINERALS EXAMINED

No.	Minerals and Groups*	Optics Measured
	Acid Carbonates	
5	Nahcolite, $NaHCO_3$—Mon. Rifle, Colo. (Am.M. 23281**)	$\alpha < 1.410$, γ: 1.582, (−)2V large
6	Trona, $Na_3H(CO_3)_2 \cdot 2H_2O$—Mon. Owens Lake, Calif.	α: 1.415, γ: 1.540, $\gamma - \alpha = 0.125$, (−)2V large
	Anhydrous Normal Carbonates	
	Calcite Group	
7	Magnesite, $MgCO_3$—Hex.R. Chewelah, Wash.	ω: 1.690, ϵ: 1.602, Uniax.(−)
8	Smithsonite, $ZnCO_3$—Hex.R. Magdalena, N. M.	ϵ: 1.730, Uniax.(−)
9	Siderite, $FeCO_3$—Hex.R. Westphalia	ϵ: 1.713, Uniax.(−)
10	Rhodochrosite, $MnCO_3$—Hex.R. Butte, Mont.	ϵ: 1.692, Uniax.(−)
11	Calcite, $CaCO_3$—Hex.R. Butte, Mont.	ω: 1.660, ϵ: 1.570, Uniax.(−)
12	Calcite, $CaCO_3$—Hex.R. Mineral Point, Wis.	ω: 1.662, ϵ: 1.568, Uniax.(−)
	Dolomite Group	
13	Dolomite, $CaMg(CO_3)_2$—Hex.R. Senator Mine, Santa Clara Co., Calif.	ω: 1.680, ϵ: 1.590, Uniax.(−)
14	Ankerite, $Ca(Fe, Mg)(CO_3)_2$—Hex.R. Brazil	ω: 1.695, ϵ: 1.602, Uniax.(−)
15	Kutnahorite, $Ca(Mn, Mg)(CO_3)_2$—Hex.R. Franklin, N. J. (Am.M. 30636)	ω: 1.742, ϵ: 1.630, Uniax.(−)
	Aragonite Group	
16	Aragonite, $CaCO_3$—Ort. Alameda Co., Calif.	α: 1.527, γ: 1.680, $\gamma - \alpha = 0.153$, (−)2V small
17	Aragonite, $CaCO_3$—Ort. Ural Mts., U.S.S.R.	α: 1.525, γ: 1.675, $\gamma - \alpha = 0.150$, (−)2V small
18	Aragonite, $CaCO_3$—Ort. Livermore, Calif.	α: 1.525, γ: 1.680, $\gamma - \alpha = 0.155$, (−)2V small
19	Strontianite, $SrCO_3$—Ort. Dreusteinfurt, Westphalia	α: 1.520, γ: 1.666, $\gamma - \alpha = 0.146$, (−)2V small
20	Witherite, $BaCO_3$—Ort. Alston Moor, England	α: 1.530, γ: 1.677, $\gamma - \alpha = 0.147$, (−)2V small
21	Cerussite, $PbCO_3$—Ort. Ibbenburen, Westphalia	$1.82 > \alpha > 1.780$, (−)2V small
	Hydrated Normal Carbonates	
22	Thermonatrite, $Na_2CO_3 \cdot H_2O$—Ort. Vesuvius, Italy	α: 1.425, γ: 1.523, $\gamma - \alpha = 0.098$
23	Pirssonite, $Na_2Ca(CO_3)_2 \cdot 2H_2O$—Ort. Searles Lake, Calif. (Am.M. 26198)	α: 1.504, γ: 1.572, $\gamma - \alpha = 0.068$, (+)2V small
24	Gaylussite, $Na_2Ca(CO_3)_2 \cdot 5H_2O$—Mon. Salt Pen, Pretoria	α: 1.450, γ: 1.520, $\gamma - \alpha = 0.070$, Biax.(−)
25	Gaylussite, $Na_2Ca(CO_3)_2 \cdot 5H_2O$—Mon. Ragtown, Nev.	α: 1.450, γ: 1.520, $\gamma - \alpha = 0.070$, Biax.(−)
26	Schroeckingerite, $NaCa_3(UO_2)(CO_3)_3(SO_4)F \cdot 10H_2O$—Ort. Lost Creek, Wamsutter, Wyo.	α: 1.493, γ: 1.540, $\gamma - \alpha = 0.047$, (−)2V small
27	Andersonite, $Na_2Ca(UO_2)(CO_3)_3 \cdot 6H_2O$—Hex.R. Atomic King No. 2, near Moab, Utah (Nat.M. 107414†)	γ: 1.522, ϵ: 1.540, $\epsilon - \omega = 0.018$, Uniax.(+)
	Carbonates with Hydroxyl or Halogen	
28	Zaratite, $Ni_3(CO_3)(OH)_4 \cdot 4H_2O$—Iso.? Wood's Mine, Penn.	n: 1.588–1.600, some show double refraction
29	Malachite, $Cu_2(CO_3)(OH)_2$—Mon. Globe, Ariz.	α: 1.650
30	Azurite, $Cu_3(CO_3)_2(OH)_2$—Mon. Copper Queen, Ariz.	α: 1.728, $\gamma > 1.83$
31	Northupite, $Na_3Mg(CO_3)_2Cl$—Iso. Searles Lake, Calif. (Am.M. 22041)	n: 1.513

* Unless otherwise indicated specimens are from the Columbia University collection. Groups are after Palache, C., Berman, H., and Frondel, C. (1951), The system of mineralogy, 2, 7th ed., John Wiley & Sons, Inc., New York, 132.

** Am.M.: American Museum of Natural History, New York.

† Nat.M.: United States National Museum, Washington, D. C.

ϵ: Index on cleavage.

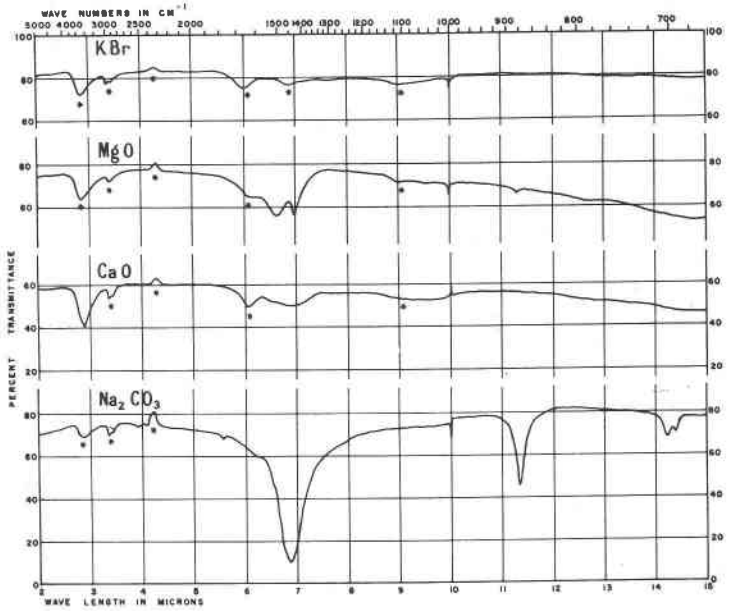

FIG. 1. Infrared spectra of reference chemical compounds.

spectrophotometer, using a NaCl prism through the spectral range 2 to 15 microns.

The method of sample preparation for infrared examination corresponds to the procedure by French et al. (1954) using the pressed pellet technique. In order to reduce light scattering, which causes a decrease in transmission and the degree of resolution, each sample was ground to less than 300 mesh in an agate mortar. A 400 to 500 mg. KBr plate, 13 mm. in diameter and 1 mm. thick, containing 1–2 mg. of the sample and compressed under a force of 2,200 lbs. on a disc 13 mm. in diameter, was found to be most satisfactory.

INFRARED SPECTRA

Reference chemical compounds

The spectra of the significant reference compounds KBr, MgO, CaO, and Na_2CO_3 are compared in Fig. 1, while the approximate numerical positions of absorption bands and corresponding intensities of absorption are listed in Table 2. Potassium bromide shows six absorption bands of medium to weak intensity, which include peaks at 2.85 and 6.00 microns caused by absorbed moisture, also two small shoulders at 4.15 and 4.35 microns. In the infrared curves shown, where KBr is used as a

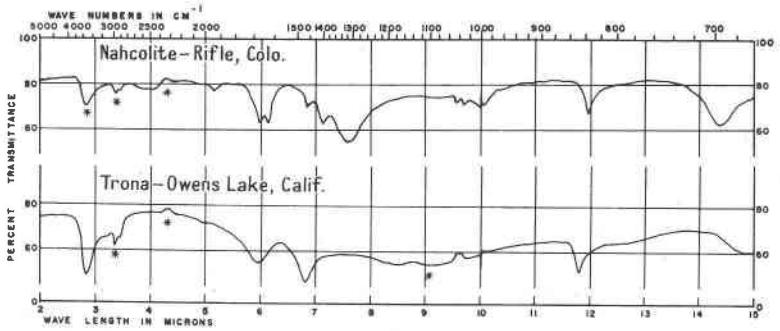

FIG. 2. Infrared spectra of acid carbonates.

mounting medium, the corresponding effects are eliminated in the tables and the peaks influenced in the graphs are marked with asterisks.

Magnesium oxide has sharp absorption peaks at 6.70 and 7.00 microns and weak bands at 11.30 and 12.50 microns (Fig. 1). Calcium oxide shows a single weak broad band at 6.70–7.00 microns, with a strong peak at 2.85 microns caused by absorbed water. The spectra of magnesite and calcite (Fig. 3) show that bands characteristic of the oxides are weak or absent, indicating a greater influence on the curves of infrared active CO_3 groups. Sodium carbonate shows strong absorption at 6.90 and 11.35 microns and weak bands at 3.95, 5.57, 14.25, and 14.40 microns caused by CO_3, which suggest the spectra of the aragonite group (Fig. 4).

TABLE 2. ABSORPTION BANDS OF THE REFERENCE CHEMICAL COMPOUNDS

No.	Chem. Compound	Positions of Absorption Bands*													
1	KBr	2.85M 3510	3.35W 2990 3.45W 2900	4.15W 2410 4.35W 2300		6.00W 1667 6.87W 1456		9.02W 1110							
2	MgO					6.70M 1493	7.00M 1429			11.30W 885	12.50W 800				
3	CaO	2.85S 3510				6.70– 1493–	7.00W 1429								
4	Na_2CO_3		3.95W 2530		5.57W 1795	6.90S 1450				11.35S 881			14.25W 702 14.40W 694		

* Wave numbers (cm^{-1}) are given below the corresponding wave length values (μ). S: strong, M: medium, W: weak.

Acid carbonates

In this group the spectra of nahcolite and trona show a partial similarity in absorption, although the structural relationships between the two are not well known (Fig. 2 and Table 3). In trona, two strong peaks caused by water of crystallization appear at 2.83 and 5.92 microns. In nahcolite, which has no molecular water, double maxima occur around 6 microns, which suggest some hydration during sample preparation (Keller et al., 1952). Absorption bands caused by the HCO_3 groups seem to occur near 5 and 7 microns, in addition to those near 10, 12, and 14 microns (Miller et al., 1952).

TABLE 3. ABSORPTION BANDS OF THE ACID CARBONATES

No.	Mineral	Positions of Absorption Bands					
5	Nahcolite	5.15W	6.13M	7.10M	9.55W	11.95M	14.40S
		1940	1630	1409	1047	837	694
		5.97M	6.85W	7.60S	9.66W		
		1675	1460	1316	1035		
6	Trona	2.83S	5.92M	6.80S	9.45W	11.75M	14.70M–
					1058		
					9.65W		
		3530	1690	1472	1037	851	681–

Calcite and dolomite groups

The infrared spectra of the calcite and dolomite groups are characterized by three prominent absorption maxima at 6.90–6.97, 11.28–11.55, and 13.36–14.02 microns and two minor peaks at 3.92–3.97 and 5.47–5.52 microns, as shown in Fig. 3 and Table 4. These bands are all considered to be caused by the CO_3 groups in the crystals. Although the minor absorption bands are poorly expressed in some spectra, they appear when satisfactory resolution is achieved. The consistent character of the infrared spectrum for a mineral species is illustrated by the two samples of calcite from different localities, which show essentially identical absorption bands. Halford (1946) has determined from an analysis of space group characteristics the existence of four molecular frequencies for the CO_3 ions in calcite, of which three are active in the infrared spectrum, also of six infrared active molecular frequencies in aragonite.

The similarity of the minerals of the dolomite group to the calcite group in atomic structure (Bragg, 1914; 1937; Wyckoff and Merwin, 1924) is reflected in the infrared spectra indicated above, as well as two absorption bands of dolomite between 11 and 12, and 13 and 14 microns

TABLE 4. ABSORPTION BANDS OF THE CALCITE AND DOLOMITE GROUPS

No.	Mineral	Positions of Absorption Bands						
7	Magnesite		5.50W 1818	6.90S 1450		11.28S 887	13.36M 748	
8	Smithsonite	3.95W 2530	5.47W 1830	6.95S 1440		11.50S 870	13.45M 743	
9	Siderite		5.50W 1818		7.03S 1422	11.55S 866	13.58M 737	
10	Rhodochrosite	3.95W 2530	5.52W 1810	6.98S 1433		11.53S 867	13.76M 727	
11	Calcite	3.93W 2545	5.52W 1812	6.97S 1435		11.42S 876		14.03M 712
12	Calcite	3.92W 2550	5.50W 1818	6.97S 1435		11.40S 878		14.02M 713
13	Dolomite	3.95W 2530	5.50W 1818	6.90S 1450		11.35S 881	13.70M 730	
14	Ankerite	3.95W 2530	5.48W 1825	6.90S 1450		11.40S 877	13.77M 726	
15	Kutnahorite	3.97W 2520	5.50W 1818	6.97S 1435		11.50S 869	13.87M 721	

which lie between those of calcite and magnesite. These two absorption bands appear to be shifted to longer wave lengths as the divalent cations in the mineral increase in atomic radius, in the order magnesite, smithsonite, siderite, rhodochrosite, and calcite in the calcite group, and dolomite, ankerite, and kutnahorite in the dolomite group (Fig. 3). This relationship has been mentioned by Adler et al. (1950) and Keller et al. (1952). The bands between 13 and 14 microns are the most diagnostic and have been applied in both qualitative and quantitative determination of the mineral constituents of rocks (Hunt and Turner, 1953). It is conceivable that the longer inter-atomic distances caused by larger cations may result in lower frequencies, that is, longer wave lengths.

Aragonite group

In the minerals of the aragonite group, major absorption peaks appear at 6.70–7.13, 11.40–11.90, and 14.03–14.77 microns, and minor bands at

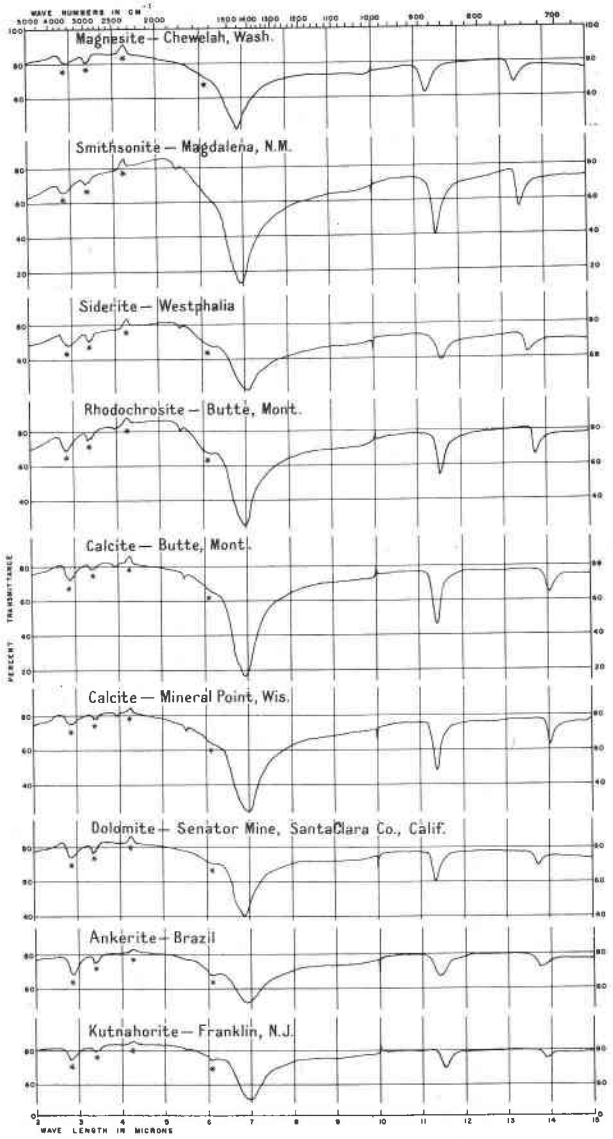

FIG. 3. Infrared spectra of the calcite and dolomite groups.

3.93–4.00, 5.53–5.75, and 9.22–9.48 microns (Fig. 4 and Table 5). The absorption bands between 11 and 12 and between 14 and 15 microns show double maxima in aragonite, but only one peak in witherite and cerussite. Strontianite has one peak at 11–12 microns and double bands at 14–15

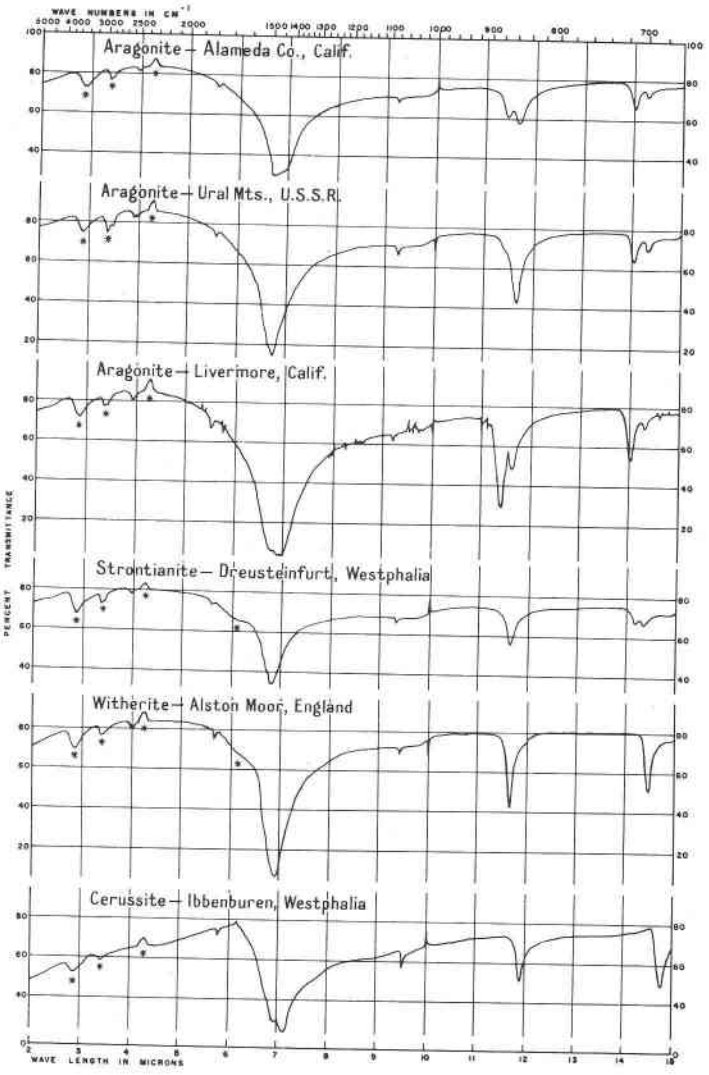

FIG. 4. Infrared spectra of the aragonite group.

microns, somewhat intermediate between aragonite and witherite. The strongest band near 7 microns appears essentially as a broad band in aragonite, and splits into two peaks in cerussite. Three spectra of aragonite from different localities are consistent in major features, although they differ moderately in the intensity of absorption in some maxima. Minute protuberances in the curve of aragonite from Livermore, Califor-

TABLE 5. ABSORPTION BANDS OF THE ARAGONITE GROUP

No.	Mineral	Positions of Absorption Bands						
16	Aragonite	3.95W 2530		5.55W 1803	6.70 –7.00S 1493 –1429	9.22W 1085	11.42M 875 11.63S 860	14.03M 712 14.30W 699
17	Aragonite	3.95W 2530		5.55W 1803	6.72S 1490	9.22W 1085	11.40W 87 11.63S 860	14.03M 712 14.30W 699
18	Aragonite	3.93W 2545		5.53W 1808	6.70 –7.00S 1493 –1429	9.22W 1085	11.42S 875 11.63M 860	14.03M 712 14.30 699
19	Strontianite	3.97W 2520		5.57W 1795	6.80S 1470	9.30W 1075	11.63S 860	14.15W 707 14.30W 699
20	Witherite		4.00W 2500	5.65W 1770	6.92S 1445	9.40W 1064	11.63S 860	14.43S 693
21	Cerussite			5.75W 1740	6.95S 7.13S 1440 1404	9.48W 1055	11.90M 841	14.77S 677

nia are probably caused by impurities. The infrared spectra obtained on common carbonates by previous workers (Adler et al., 1950; Keller et al., 1952) show somewhat different positions for the absorption bands, but the minor peaks are incompletely shown, which may be attributed to the purity of the samples or the sensitivity of the instrument.

The shift of the absorption bands is more apparent than in the calcite and dolomite groups. Apparently it follows the sequence of increase in atomic weight rather than atomic radius. The strong bands in the areas 11–12 and 14–15 microns and also other maxima, including even minor peaks, are shifted to longer wave lengths, as the cations in the mineral become heavier, in the order of aragonite, strontianite, witherite, and cerussite. Also, the larger cations of the minerals of this group cause the absorption bands to occur at longer wave lengths between 14 and 15, rather than between 13 and 14 microns, as in the calcite-dolomite group. The condition that larger atomic masses may yield to longer wave lengths arises from the equation

$$v = \frac{i}{2\pi c}\sqrt{\frac{k}{u}},$$

where v = frequency of vibration in cm^{-1}, c = velocity of light, u = reduced mass of the vibrating atoms, k = force constant (Barnes et al., 1944).

A comparison of the spectra indicates that the positions of the absorption bands are affected by the cations present, but the spectra are dominated by the CO_3 groups. In the spectra of a calcite and dolomite groups, the weak absorption bands between 9 and 10 microns are absent, and no double peaks appear. This difference may be explained by the structural

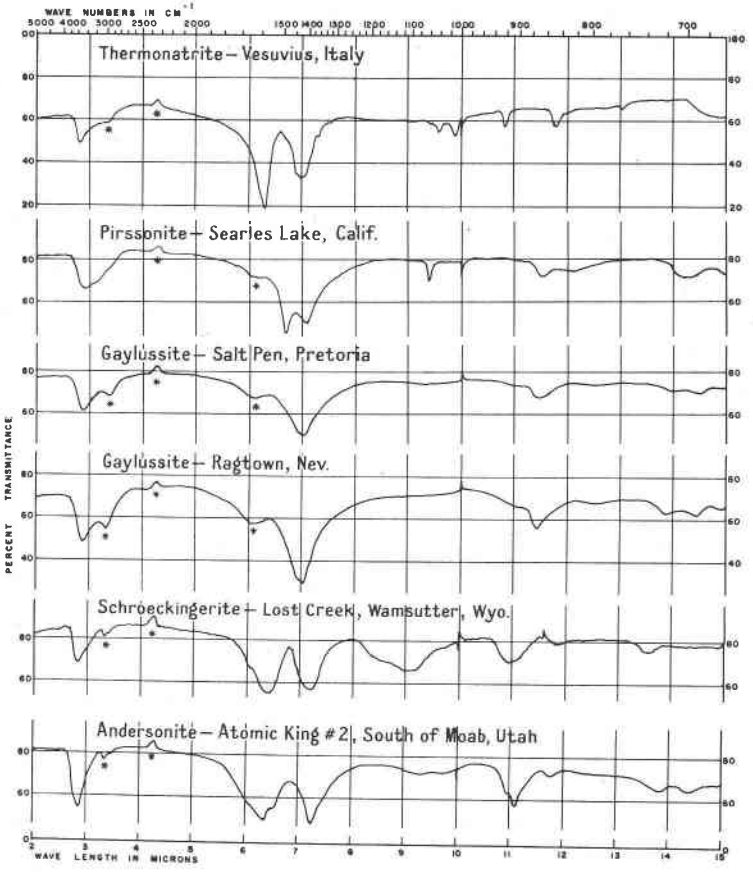

FIG. 5. Infrared spectra of hydrated normal carbonates.

difference, since in rhombohedral calcite the CO_3 group is placed so that each oxygen atom is in contact with two calcium atoms, while in orthorhombic aragonite each oxygen atom is in contact with three calcium atoms (Bragg, 1937; Adler et al., 1950; Keller et al., 1952).

Observations on carbonate mixtures were made by Keller et al. (1952) on artificial mixtures of calcite with aragonite, and calcite with magnesite. The curves of the mixtures were noted to contain all the peaks

characteristic of the spectrum of each individual constituent. However, differences were observed between the spectra of dolomite and a calcite-magnesite mixture, since the former is a distinct mineral species, while the latter is a mechanical mixture.

Hydrated normal carbonates

The infrared spectra of the hydrated normal carbonates (Fig. 5 and Table 6) are characterized by a range in position and intensity of bands caused by H_2O molecules. The absorption peaks caused by water of crystallization are shown at 2.82–2.90 and 6.28–6.52 microns, and the

TABLE 6. ABSORPTION BANDS OF THE HYDRATED NORMAL CARBONATES

No.	Mineral	Positions of Absorption Bands								
22	Thermonatrite	2.82M 3540	6.28S 1592	7.00S 1429 7.28W 1373		9.57W 1045 9.85W 1016	10.82W 924	11.75W 851	13.02W 768	
23	Pirssonite	2.85M 3510	6.70S 1493	7.05S 1419		9.35W 1070		11.53W 867		14.25W 702
24	Gaylussite	2.85M 3510		7.05S 1419				11.45W 873	13.92W 718	14.48W 691
25	Gaylussite	2.90S 3450		7.05S 1419				11.42M 876	13.92W 718	14.45W 692
26	Schroeckingerite	2.85M 3510	6.42S 1558	7.20S 1390	8.62W 1160	9.12M 1098	10.95M 913	11.85W 844	13.55W 738	
27	Andersonite	2.85S 3510	6.33S 1580 6.52M 1535	7.22S 1385		9.27W 1080	10.95M 913	11.10S 901 11.80W 848	13.75W 727	14.35W 697

maxima attributed to the CO_3 groups at 6.70–7.22 and between 11 and 15 microns. In addition, a characteristic absorption band caused by the SO_4 radical appears at 9.12 microns in schroeckingerite. A silicate impurity appears to have been present in the samples of thermonatrite and pirssonite, resulting in small peaks between 9 and 11 microns (Miller et al., 1952; Keller et al., 1952). The two spectra of gaylussite from different localities show closely similar absorption bands.

The carbonate minerals of this group are more complicated in chemical composition and crystal structure, and the relationships between the infrared spectra and atomic structure are not well known. However, the similarity of schroeckingerite and andersonite in infrared spectra suggests a possible structural analogy between the two uranium minerals. Schroeckingerite is orthorhombic, pseudo-hexagonal in form (Hurlbut,

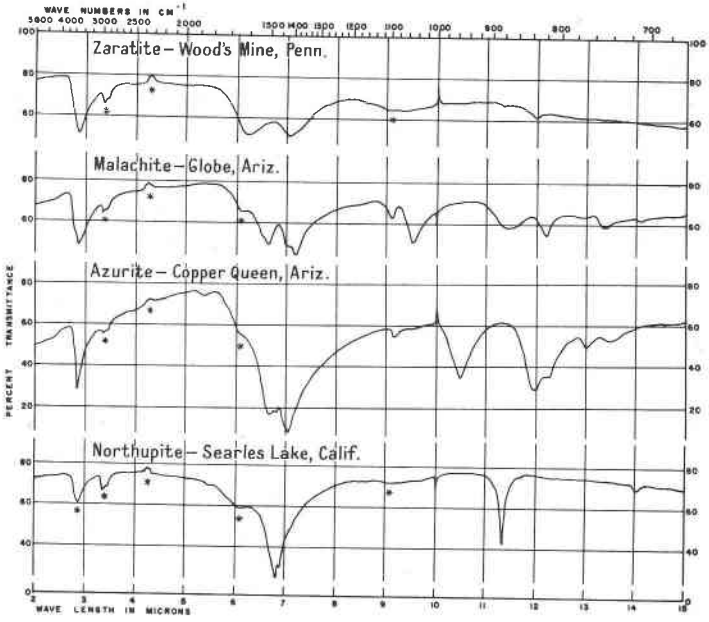

FIG. 6. Infrared spectra of carbonates containing hydroxyl or halogen.

1954), and andersonite shows a rhombohedral lattice (Axelrod et al., 1951). Infrared curves are somewhat alike, but the *X*-ray diffraction patterns differ.

Carbonates containing hydroxyl or halogen

The absorption bands of four representatives of this group, zaratite, malachite, azurite, and northupite, are shown in Fig. 6 and Table 7. Characteristic strong maxima due to hydrogen bonds (Keller and Pickett, 1950) appear at 2.85 microns. In zaratite a band caused by water of crystallization occurs at 6.25 microns, in addition to a band caused by hydroxyl bonding. The absorption bands caused by the CO_3 groups occur chiefly near 7 microns as strong peaks and at wave lengths longer than 9 microns as two or more maxima of varying intensity. In azurite and northupite a weak band occurs at 5.40–5.47 microns, comparable to bands yielded by the minerals of the calcite and dolomite groups, while in malachite and azurite a weak peak occurs at 9.10–9.15 microns similar to the bands given by the minerals of the aragonite group (see Figs. 3 and 4).

The spectral relation to crystal structure is not well known among the minerals of this group. Malachite belongs to the space group $P2_1/a$ (Ramsdell and Wolfe, 1950), and azurite to $P2_1/c$ (Brasseur, 1932). The

TABLE 7. ABSORPTION BANDS OF THE CARBONATES CONTAINING HYDROXYL OR HALOGEN

No.	Mineral	Positions of Absorption Bands									
28	Zaratite	2.85S 3510		6.25S 1600	7.05S 1419			11.35W 881 11.97W 835			
29	Malachite	2.85S 3510		6.62S 1510	7.00M 1430 7.17S 1395	9.10W 1099 9.52S 1050		11.45M 873	12.17M 822 12.90W 775	13.33W 750	14.05W 712
30	Azurite	2.84S 3520	5.40W 1852	6.63S 1509 6.78W 1475	7.03S 1422	9.15W 1093	10.47S 955	11.97S 835	12.23M 817	13.00W 769 13.45W 743	
31	Northupite		5.47W 1830	6.78S 1475 6.85S 1461				11.33S 882			14.02W 713

general similarity in crystal structure which at the same time includes minor differences is reflected in the infrared spectra. The absorption bands of northupite correspond to those of the calcite and dolomite groups, except for the doublet near 7 microns. It is worthy of note that the bands at 11.33 and 14.02 microns are located between corresponding bands for sodium carbonate and magnesite (see Figs. 1 and 3). The influence of chlorine on the spectrum appears to be subordinate, as in the case of the cations.

CONCLUSION

The infrared spectra of the calcite and dolomite groups are characterized by three major and two minor absorption bands attributed to CO_3, while those of the aragonite group exhibit three to five major and three minor peaks, according to the difference in crystal structure. There is also a definite relation between band shift and the atomic radius or mass of the cations contained in these isomorphous groups.

The minerals of other groups are more complicated in chemical composition and crystal structure, and the mutual spectral relationships are as yet indefinite. However, the absorption bands caused by the infrared active groups, such as CO_3, HCO_3, H_2O, OH, and SO_4, are revealed, and the spectrum is diagnostic for each mineral.

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