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THE INFRARED SPECTRUM OF DAWSONITE

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INTRODUCTION

As part of a broad program on minerals research by the U.S. Bureau of Mines, infrared spectroscopy is being used at its Morgantown, W. Va., laboratories for the study of various minerals of current interest to both Government and industry. One of these is the mineral dawsonite, a basic carbonate of sodium and aluminum, $NaAl(CO_3)(OH)_2$. A recent report (Smith and Milton, 1966) describes relatively abundant deposits of this mineral as a rock-forming constituent of oil shale in the Piceance Creek Basin of northwestern Colorado. This occurrence has created interest in dawsonite as a potential ore of aluminum. In addition, alkalized alumina (synthetic dawsonite) prepared by the reaction of aluminum sulfate and sodium carbonate, is being tested by the Bureau of Mines as an absorbent for sulfur dioxide in flue gas. This note presents the infrared spectrum of pure natural dawsonite, compares it qualitatively with synthetic dawsonite, and demonstrates that infrared spectroscopy to 200 cm^{-1} is a reliable method for the identification and possible quantitative analysis of this mineral.

EXPERIMENTAL

Dawsonite is a colorless to white transparent mineral and occurs as rosettes of bladed to acicular crystals (0.05–0.5 mm) (Stevenson and Stevenson, 1965), as thin incrustations, or as sedimentary nodular accretions. A few milligrams of pure dawsonite were isolated microscopically (40–100×) from each of the three sources shown in Table 1. The relative hardness of 3 for dawsonite greatly facilitated its isolation from the matrix minerals. About 0.5 mg of the isolated sample was weighed on a microbalance, ground for 5 minutes with 500 mg of cesium iodide in an agate ball mill and this mixture pressed into a 0.8×13 mm pellet. The infrared spectrum was then scanned on a Perkin-Elmer 621 infrared grating spectrophotometer purged with dry air. This instrument extends the range of the mid-infrared from 650 to 200 cm^{-1}, adding several useful absorption bands to the infrared spectrum of many minerals (Karr, *et al.*, 1967). The associated minerals and matrices listed in Table 1 were also identified by their infrared spectra and the dawsonite spectrum for each specimen checked for possible contamination from these minerals. The spectra were also examined for evidence of other known accessory minerals peculiar to the various localities (Hay, 1963; Palache, *et al.*, 1951; Smith and Milton, 1966; Stevenson and Stevenson, 1965).

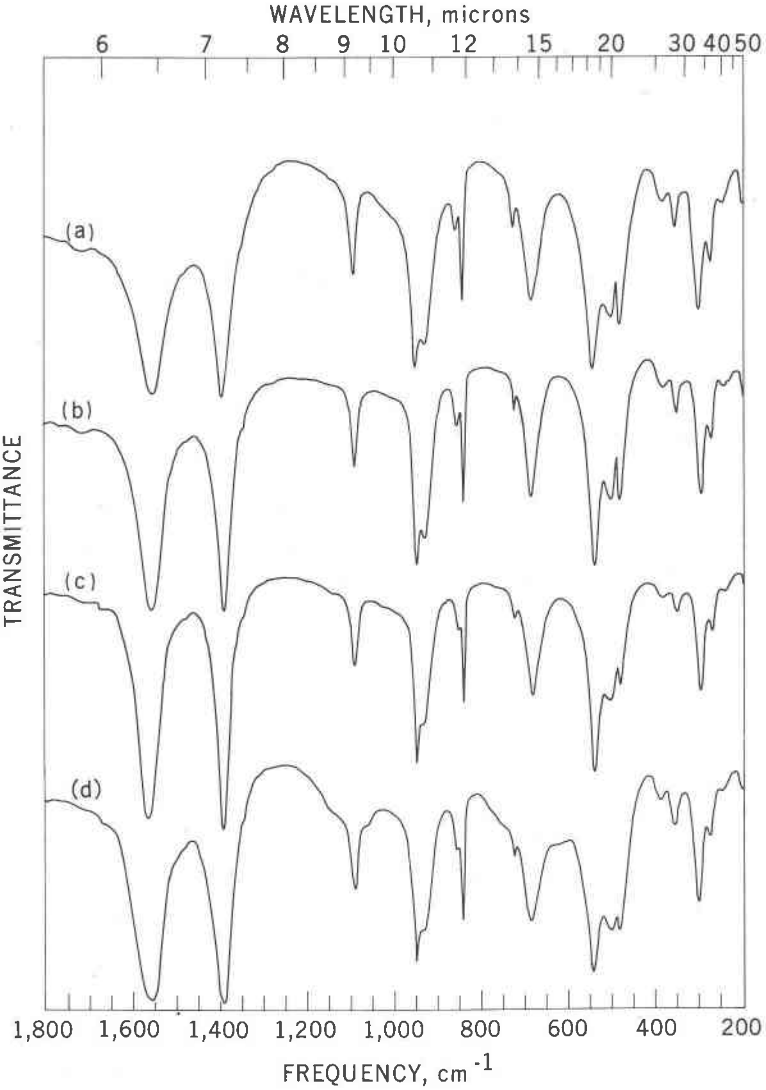
TABLE 1. DAWSONITE SAMPLE DESCRIPTIONS

Locality	Source	Description and associated materials
McGill University, Montreal, Canada	Mrs. Louise S. Stevenson, Redpath Museum, Montreal Canada	Bladed crystals and rosettes coating the joint plane of a feldspathic dike. Specimen size: 3″×1½″
Komana, northern Albania	Ward's Natural Science Establishment, Inc., Rochester, N. Y.	Rosettes of acicular crystals associated with realgar on host of silica. Specimen size: 1″×1½″
Olduvai Gorge, Tanzania	Dr. Charles Milton, George Washington University, Washington, D. C.	Sedimentary nodular accretions (up to 1/4″), encrusted with clay

The purities of the three dawsonite specimens were further substantiated by X-ray diffraction. Spacings on the patterns agreed well with the ASTM Powder Diffraction File, Card 12-449, except for some line intensity differences.

RESULTS AND DISCUSSION

Infrared spectra for dawsonite from the three localities are shown in Figure 1 and the absorption bands listed in Table 2. The agreement, in both frequencies and relative intensities, supports the authenticity of the infrared data. The two strong bands at 3280 cm^{-1} and 1555 cm^{-1} can be assigned to O-H stretching and bending vibrations, respectively. The position of the O-H stretch indicates that hydrogen bonding contributes to the cohesive forces of the crystal lattice. The strong band at 1390 cm^{-1} can be assigned to the asymmetric stretching vibrations



(a) Montreal, Canada
(b) N. Albania
(c) E. Africa
(d) Synthetic

FIG. 1. Infrared spectra of natural and synthetic Dawsonite.

(ν_3) of the CO_3 radical. It occurs at a frequency somewhat lower than the range for a large number of normal inorganic carbonates (1450 to 1410 cm^{-1}) (Bellamy, 1958) and carbonate minerals (Adler and Kerr, 1963).

The identification and quantitative estimation of dawsonite by the infrared method in the presence of commonly occurring accessory minerals is highly favorable as was shown by a study of the infrared spectra of a number of these minerals. The two strongest bands of dawsonite at 1390 cm^{-1} and 1555 cm^{-1} occur in a region not seriously overlapped by the principal bands of sulfates (1130 to 1080 cm^{-1}), silicates (1100 to 900 cm^{-1}), phosphates (1100 to 1000 cm^{-1}), nitrates (1380 to 1350 cm^{-1}) (Bellamy, 1958), and clays (1100 to 1000 cm^{-1}). Sulfides and oxides generally have absorption bands at lower frequencies. We examined the infrared spectra of samples of dawsonite-bearing oil shales from Colorado. These spectra showed strong bands for dawsonite, dolomite, microcline, and quartz, and weak organic bands. The presence of the organic matter made it extremely difficult to isolate pure dawsonite microscopically from this source. The development of a successful quantitative procedure for the estimation of dawsonite in these and other mixtures, however, is contingent on obtaining enough pure mineral as a standard so that studies can be conducted on particle size reduction versus absorptivity. From band intensity measurements on the isolated pure mineral, we estimate that amounts as small as 1 to 3 weight-percent can be detected in mixtures, compared to a recently published estimation of X-ray detectability at 3 percent (Smith and Milton, 1966).

TABLE 2. INFRARED ABSORPTION BANDS OF NATURAL DAWSONITE

Frequency, cm^{-1} (relative intensity)[1]		
245 (w)	539 (m)	1090 (m)
274 (w)	685 (m)	1350 (vw)
297 (m)	723 (w)	1390 (s)
354 (w)	840 (m)	1480 (vw)
385 (w)	856 (w)	1555 (s)
482 (m)	928 (m)	3280 (s)
503 (m)	948 (m)	3450 (w)

[1] s=strong, m=medium, w=weak, vw=very weak.

Synthetic dawsonite, prepared by W. R. Grace and Co., Baltimore, Md., was examined and its spectrum (curve d, Figure 1) showed good agreement with that of natural dawsonite. The X-ray data for this sample also agreed well with that of natural dawsonite. However, the lines for the synthetic material were more diffuse and no back reflection lines were recorded, indicating a difference in the degree of crystallinity of the two materials.

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RELATIONS OF THE MANGANESE-CALCIUM SILICATES, GAGEITE AND HARSTIGITE

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INTRODUCTION

A systematic study on the crystal chemistry of manganese silicates prompted further investigations on gageite and harstigite, two rare and poorly understood species. These studies indicate that the two minerals are structurally related but their unusual compositions are difficult to interpret without recourse to crystal structure analysis.

GAGEITE

Gageite was frequently found during mining at Franklin, Sussex County, New Jersey, its only reported locality, though it could hardly