TABLE 2. ANALYTICAL LINES

| Analytical Line | Internal Standard Line |
|---|---|
| Ce 4133.80 | Sc 4023.68 |
| Eu 4129.73 | |
| Pr 4100.74 | |
| Nd 4023.00 | |
| Th 3469.92 | |
| Tm 3462.20 | Sc 3359.67 |
| Ho 3456.00 | |
| Er 3364.09 | |
| Gd 3350.48 | |
| Y 3330.88 | |
| Tb 3324.40 | |
| Dy 3319.88 | |
| Sm 3306.37 | |
| La 3303.11 | |
| Lu 3281.74 | |
| Yb 3192.87 | |

In the light of the new data presented above it must be assumed that this may have a very appreciable effect on the calculated stoichiometries.

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# THE PROBLEM OF STACKING-ORDER IN NATURAL HYDROZINCITE

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In 1958 the author published the results of his chemical, optical, DTA, and *x*-ray investigation of basic zinc carbonate (hydrozincite) which formed incrustations on the planking in the Orzel Bialy mine at Brzeziny Slaskie, Upper Silesia, Poland. In a recent paper, Jambor (1964) postulated the existence of two varieties of natural basic zinc carbonate, differing slightly in their $CO_2$ and $H_2O$ contents, temperature of endothermic effect, *x*-ray powder patterns, and infrared absorption in the region of OH stretching vibrations. On the basis of the author's (Zabinski, 1958) description and $x$-ray data for the Orzel Bialy mineral, Jambor tentatively assigned it to the less common variety named by him "Dorchester type". Jambor's paper encouraged the present author to make supplementary infrared studies of the Upper Silesian hydrozincite in order to determine its exact type. Similar investigations were also made on several specimens of hydrozincite from localities not mentioned in Jambor's paper: Bleiberg, Austria; Sedmocislenici, Bulgaria; Monteponi and Raibl, Italy.

Infrared spectra were obtained with a UR-10 Zeiss spectrophotometer, using NaCl windows and a Nujol mull technique. In the region of wave numbers 500–1800 $cm^{-1}$, merely small differences in the distinctness of absorption bands of the different hydrozincites were noticed. On the other hand, in the region of OH stretching vibrations, distinct differences in the shape and maximum frequencies of corresponding bands were recorded (Fig. 1). The OH absorption band of hydrozincite from the Orzel Bialy mine (No. 2) appears as a broad peak with a maximum at about 3320 $cm^{-1}$, thus at considerably lower frequencies than that of the "Dorchester" mineral (Fig. 1, No. 1, ca 3420 $cm^{-1}$). The OH absorption band of hydrozincite from Monteponi (No. 4) is much weaker because of substantial contamination by smithsonite. The Bleiberg sample (No. 3) has a broad and distinct maximum at 3300 $cm^{-1}$, while the Raibl (No. 5) and Sedmocislenici (No. 6) minerals show a well-resolved double band with maxima at 3230 and 3300 $cm^{-1}$. The latter curves are in good agreement with those recorded by Jambor for material from Constantine, considered by him to be the more common type of hydrozincite.

Since the absorption maximum of hydrozincite from the Orzel Bialy mine appears at much lower frequencies than that of the "Dorchester" carbonate, the minerals cannot be regarded as identical. Rather, the Orzel Bialy material represents a form intermediate between the "Dorchester" and "Constantine" types, and the nature of the hydrozincite structure (Ghose, 1964) provides an explanation for its existence. Hydrozincite consists essentially of $Zn_3(OH)_6O_2^{4-}$ sheets with additional Zn atoms and $CO_3$ groups occurring above and below these sheets. Since the carbonate groups hold the sheets together, it may be assumed that a deficiency of these groups will facilitate disorder in the layer sequence. Such disorder seems to be typical of both natural and synthetic basic zinc carbonates which have been freshly precipitated. Among the synthetic carbonates, stacking-ordered and disordered modifications have been ascertained (Sahli, 1952, fide Ghose, 1964). Aging of the disordered phase, particularly in the presence of $CO_2$, may convert it to the ordered phase. The "Dorchester" mineral represents a disordered phase, while the hydrozincites from Constantine, Raibl, and Sedmocislenici are evidently ordered. The Polish hydrozincite, as well as the one from Bleiberg, has intermediate

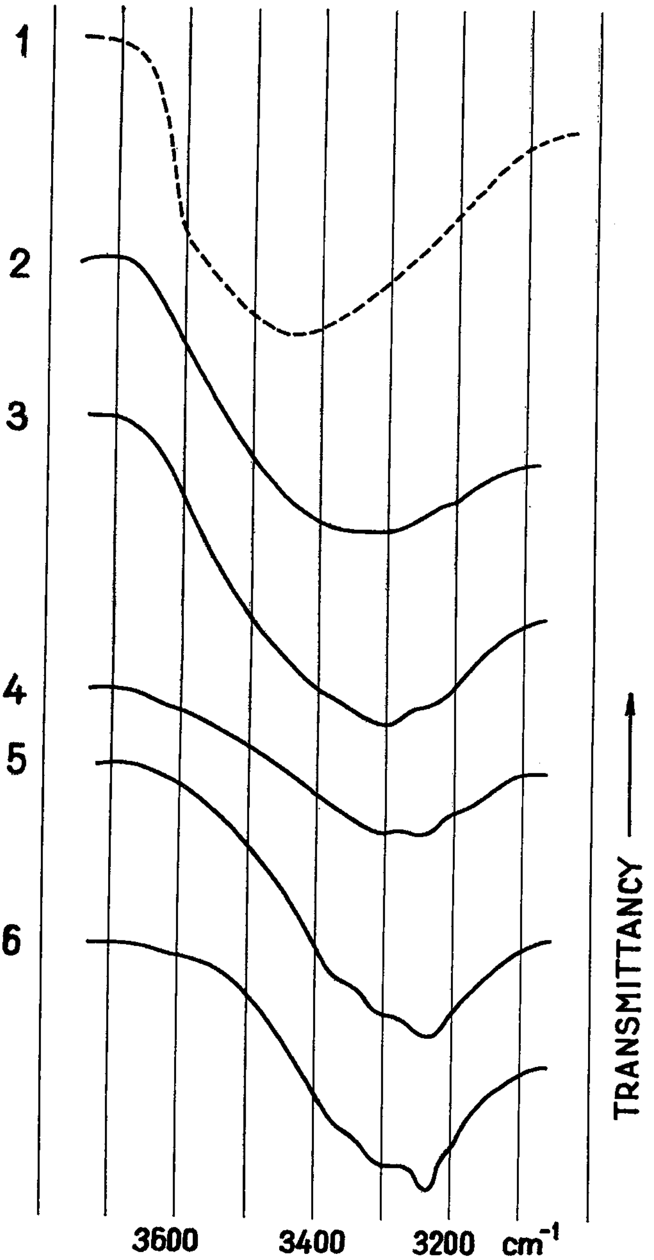

FIG. 1. Infrared absorption curves of natural hydrozincites 1—Dorchester (after Jambor 1964, up to scale), 2—Orzel Bialy mine, 3—Bleiberg, 4—Monteponi, 5—Raibl, 6—Sedmocislenici.

features. In an ordered phase the hydrogen bonds between OH and neighbouring O atoms have lengths of 2.78 and 2.90 Å, and these correspond (Ghose, 1964) to the absorption maxima at 3225 and 3290 $cm^{-1}$ respectively. When stacking-disorder increases, the hydrogen bonds become elongated by different amounts in the various sheets. The absorption band is thus broadened and its maximum shifted toward higher frequencies.

The present author's investigations give evidence of the existence in nature of a series of hydrozincites varying in stacking-order, and therefore it seems unnecessary to distinguish the Dorchester carbonate as a new mineral. It would rather be more correct to regard the different modifications of hydrozincite as members of a stacking-order series.

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# NATURAL AND SYNTHETIC HYDROZINCITES

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This writer earlier suggested (Jambor, 1964) that natural hydrozincites could be classified into two categories—hydrozincite proper, and a disordered, possibly dimorphous phase of hydrozincite referred to as the "Dorchester type". Although the writer found no difficulty in classifying the available specimens of natural zinc carbonates as hydrozincite or Dorchester types, it was concluded (1964, p. 107) that "— it is nevertheless clear that examination of additional samples by other workers will provide an immediate practical test as to the feasibility of maintaining the proposed classification". The practical test has not been long in coming.

Feitknecht & Oswald (1966) have shown that synthetic hydrozincites precipitated under carefully controlled conditions in some cases give