

## New data for lansfordite

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**ABSTRACT.** Euhedral crystals of the low-temperature mineral lansfordite,  $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ , have been prepared from saturated magnesium bicarbonate solutions at temperatures below  $10^\circ\text{C}$ . The crystals are monoclinic  $P2_1/a$  with  $a = 12.4758(7)$ ,  $b = 7.6258(4)$ ,  $c = 7.3463(6)$  Å,  $\beta = 101.762(6)^\circ$ ,  $V = 684.24$  Å<sup>3</sup>,  $D_{\text{calc.}} = 1.693$  g cm<sup>-3</sup>,  $D_{\text{obs.}} = 1.70(1)$  g m<sup>-3</sup>. At room temperature, the crystals slowly effloresce to produce pseudomorphs of nesquehonite,  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ . Dehydration is complete at  $300^\circ\text{C}$ , with decarbonation taking place in the interval to  $560^\circ\text{C}$ . A new X-ray powder diffraction pattern is presented, and details of the infra-red absorption spectrum are discussed.

THE rare mineral lansfordite occurs as short, colourless to white, prismatic crystals (fig. 1) at Nesquehoning, Carbon County, Pennsylvania, at Atlin, British Columbia, and at Cogne, Piedmont, Italy (Palache *et al.*, 1951). Associated phases include nesquehonite,  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ , and hydromagnesite,  $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ .

Following its initial discovery by Genth (1888), lansfordite received regular attention for some 50 years (see Fenoglio, 1933, and Palache *et al.*, 1951, and references therein). Since then, however, interest has been somewhat sporadic, no doubt in part because collected specimens of natural crystals were observed to have transformed to nesquehonite (White, 1971). Indeed, the JCPDS pattern attributed to lansfordite (cards 18-769 and 21-959) represents a mixture of nesquehonite and hydromagnesite and has been deleted from the file. Understandably, therefore, all recent studies of the mineral have dealt with synthetic material, primarily in regard to its phase relationships with other hydrous magnesium carbonates (Kazakov *et al.*, 1959; Langmuir, 1965; Lippmann, 1973). The present study of lansfordite is a by-product of research on the production of high-purity MgO from magnesite by the calcination/ $\text{CO}_2$ -leaching process (Canterford *et al.*, 1981) and was initiated in order to obtain details of the X-ray powder diffraction, thermal dehydration, and infrared absorption of this poorly characterized, rather ephemeral, mineral.

*Method of preparation.* High-purity MgO was prepared by calcining chromatographic-grade

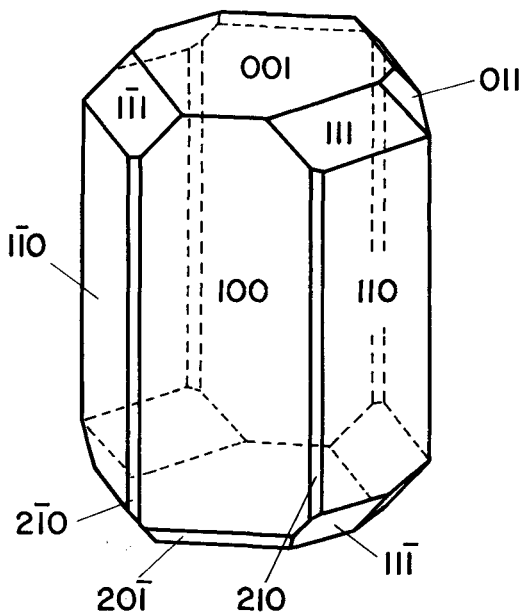


FIG. 1. Drawing of a lansfordite crystal, showing the development of typical forms (after Fenoglio, 1933).

anhydrous  $\text{MgCO}_3$  at  $700^\circ\text{C}$  for 1 h in a preheated electric muffle furnace. After being cooled to room temperature, 20 g of the MgO were slurred with 1 litre of doubly distilled water, placed in a 2-litre autoclave, and equilibrated at  $15^\circ\text{C}$ . The autoclave was then sealed and charged with high-purity  $\text{CO}_2$ , the pressure being maintained at 700 kPa. After 1 h the pressure was released and the  $\text{Mg}(\text{HCO}_3)_2$  solution was recovered and filtered through a Millipore filter with a pore size of  $0.65 \mu\text{m}$ . The solution was then placed in an open beaker and allowed to stand at a temperature of  $15^\circ\text{C}$ . After several days, numerous small prismatic crystals (of lansfordite) were observed to be growing on the walls of the beaker, with acicular crystals (of nesquehonite) growing on the solution surface. When the solution was maintained at  $0^\circ\text{C}$ , lansfordite was the only crystalline product, which is

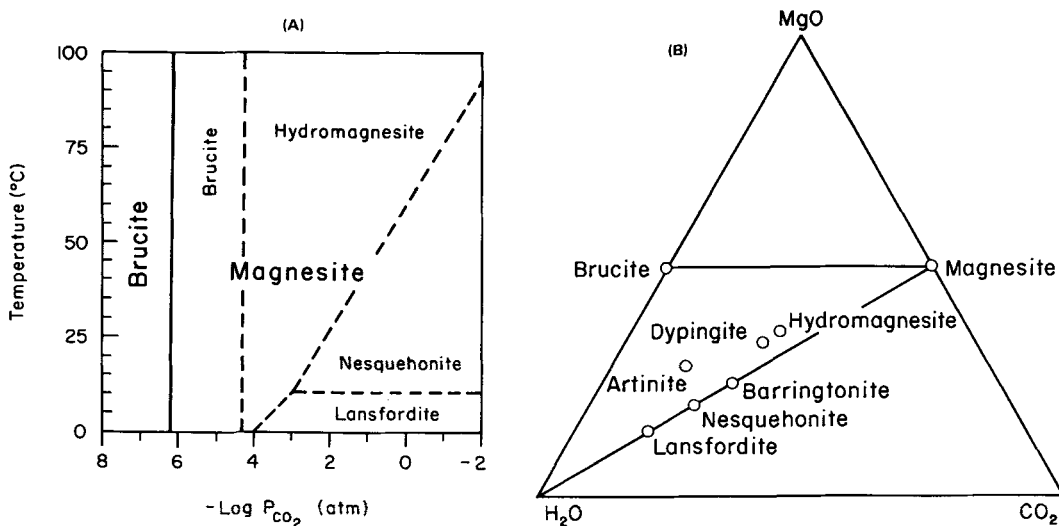


FIG. 2. Phase diagrams in the system MgO-CO<sub>2</sub>-H<sub>2</sub>O (after Lippmann, 1973, and Langmuir, 1965). In (A), metastable fields are delineated by dashed lines and are indicated by the names of the metastable phases in smaller letters.

consistent with published stability relations in the MgO-CO<sub>2</sub>-H<sub>2</sub>O system (fig. 2).

Over a period of several months, the lansfordite crystals increased to a size of about 2 mm and developed the morphology shown in fig. 1. Even larger crystals, though with reduced transparency and generally poorer quality, could be obtained by carefully suspending seed crystals in the Mg(HCO<sub>3</sub>)<sub>2</sub> solution. If the crystals were stored below about 10 °C, they could be kept indefinitely in their transparent unaltered condition. However, if they were subjected to higher temperature or reduced pressures, their surfaces became dull and opaque and masses of small, white, needle-shaped crystals began to grow inwards, eventually consuming the bulk of the larger crystal while maintaining the external lansfordite morphology (fig. 3). The white coatings and needles were identified by X-ray diffraction as randomly oriented crystals of nesquehonite. This pseudomorphous replacement is therefore a spontaneous dehydration reaction that is similar to the behaviour of epsomite, MgSO<sub>4</sub>·7H<sub>2</sub>O, melanterite, FeSO<sub>4</sub>·7H<sub>2</sub>O, and chalcantite, CuSO<sub>4</sub>·5H<sub>2</sub>O, under appropriate conditions of low humidity. The lansfordite reaction does not appear to be reversible, however.

**Unit-cell geometry and symmetry.** The crystal of lansfordite selected for study was a transparent, essentially equidimensional prism having an edge length of 0.15 mm and bounded by the forms {111}, {110}, and {100} and by the cleavage plane (001). Preliminary X-ray precession and Weissenberg photographs displayed the diffraction symmetry

$2/mP-2_1/a-$ , thereby uniquely defining the space group as monoclinic  $P2_1/a$ . This result is at variance with the symmetry inferred from morphology by Palache *et al.* (1951). The specimen was mounted on an Enraf-Nonius CAD4 four-circle automatic diffractometer in an arbitrary orientation, and the unit-cell parameters were refined by an on-line least-squares technique from the observed  $2\theta$  values of twenty-five automatically centred reflections in the range 40–52°, measured at 20 °C with graphite-monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). The resultant cell dimensions— $a = 12.4758(7)$ ,  $b = 7.6258(4)$ ,  $c = 7.3463(6) \text{ \AA}$ ,  $\beta = 101.762(6)^\circ$  ( $\alpha$  and  $\gamma$  were statistically identical to 90°),  $V = 684.24 \text{ \AA}^3$ —agree well with those determined by Fenoglio (1933).

Density measurements were made by volume displacement (in toluene), using several samples in the range 10–25 mg. The results yielded a value of  $D_{\text{obs.}} = 1.70(1) \text{ g cm}^{-3}$ . The density calculated from the lansfordite ideal formula and a  $Z$  value of 4 is  $1.693 \text{ g cm}^{-3}$ .

**X-ray powder diffraction data.** X-ray powder diffraction data were obtained at 22 °C on a standard Philips diffractometer, using a diffracted-beam focusing graphite monochromator and Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). A second set of unit-cell dimensions was obtained from these data by least-squares fitting (Stewart, 1978) of the calculated to the observed  $d$  spacings (Table I), with the incorporation of a  $2\theta$ -zero parameter to compensate for a diffractometer eccentricity of  $-0.07(2)^\circ$ . Only the unambiguously indexed reflec-

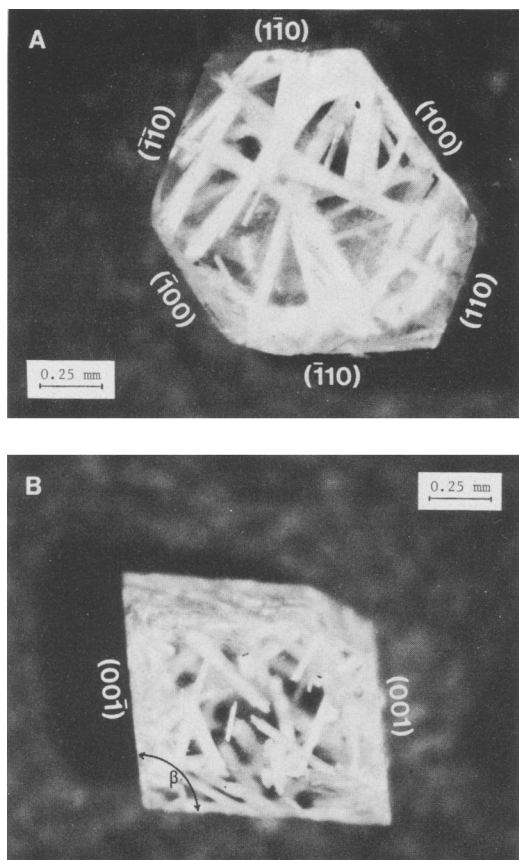


FIG. 3. Single crystal of lansfordite viewed (A) down the *c*-axis and (B) approximately down the *b*-axis, showing clusters of nesquehonite needles growing from the surface of the lansfordite into the bulk of the crystal in random orientations. The Miller indices of the faces are indicated in (A), and the  $\beta$  angle in (B) is  $101^\circ$ .

tions were included in the refinement, with 50% weights assigned to those with low-intensity, broad profiles. Problems of multiple indexing were reduced by reference to a set of single-crystal intensities collected for later structure analysis. The resultant cell dimensions— $a = 12.463(5)$ ,  $b = 7.610(3)$ ,  $c = 7.340(3)$  Å,  $\beta = 101.76(3)^\circ$ —agree closely with those obtained from the single-crystal study, thereby confirming the reflection indices assigned in Table I.

**Thermal analysis.** The thermal properties of very lightly ground lansfordite were measured on a Rigaku simultaneous DTA/TGA thermo-analyser, using AR-grade  $\alpha$ - $\text{Al}_2\text{O}_3$  as the reference material and a sample weight of 11.23 mg. The behaviour of the sample was measured from room tempera-

Table I. X-ray powder diffraction data for lansfordite

<i>h</i>	<i>k</i>	<i>l</i>	$d_{\text{calc.}}$	$d_{\text{obs.}}$	$I/I_0$	<i>h</i>	<i>k</i>	<i>l</i>	$d_{\text{calc.}}$	$d_{\text{obs.}}$	$I/I_0$
0	0	1	7.192	7.178	30	1	3	2	2.008		
2	0	0	6.107	6.120	12	3	3	1	2.007	2.008	15
0	1	1	5.232	5.239	31	4	3	0	1.954		
2	0	-1	5.208			4	3	-1	1.951		
1	1	-1	5.090	5.110	31	6	0	-2	1.950	1.950	3
2	1	0	4.767	4.782	15	1	2	3	1.948		
1	1	1	4.570	4.583	95	0	4	0	1.906	1.908	21
2	1	-1	4.301	4.310	21	6	1	-2	1.889	1.886	6
2	0	1	4.247	4.257	2	1	4	0	1.884		
0	2	0	3.813	3.818	3	5	1	-3	1.860	1.861	8
2	1	1	3.711	3.712	6	4	2	2	1.855	1.848	3
1	2	0	3.640	3.645	2	3	1	3	1.847	1.843	4
0	0	2	3.596	3.597	14	0	4	1	1.843	1.843	4
3	1	-1	3.472	3.479	2	4	3	1	1.826	1.820	6
2	0	-2	3.418	3.424	3	2	4	0	1.820	1.800	12
0	2	1	3.369	3.369	4	0	0	4	1.798		
1	2	-1	3.330	3.336	10	6	2	0	1.794	1.792	2
2	2	0	3.234	3.237	55	2	4	-1	1.790	1.772	7
1	2	1	3.171	3.169	2	5	3	-1	1.772	1.752	1
2	2	-1	3.077	3.071	3	0	1	4	1.750	1.736	9
4	0	-1	3.043	3.047	5	6	2	-2	1.736	1.736	1
1	1	2	3.008	3.014	25	-1	1	2	1.734	1.710	33
2	0	2	2.855			4	0	-4	1.709	1.695	4
2	2	1	2.837	2.839	100	3	3	-3	1.697	1.651	6
4	1	-1	2.826			1	3	3	1.692	1.634	2
3	1	-2	2.806	2.812	7	2	2	-4	1.649	1.616	2
3	2	0	2.783	2.785	24	2	0	4	1.637	1.600	4
3	2	-1	2.726	2.732	2	6	0	2	1.634	1.616	2
2	1	2	2.674	2.674	2	4	4	0	1.617	1.600	4
4	0	1	2.625			4	4	-1	1.616	1.600	4
0	2	2	2.616	2.616	5	7	2	-1	1.614	1.600	4
4	0	-2	2.604			6	1	2	1.598	1.593	4
2	2	-2	2.545	2.548	22	2	2	4	1.504	1.503	4
1	3	0	2.489			6	2	2	1.502	1.503	4
4	1	1	2.482	2.485	15	5	2	1	1.502	1.488	2
3	2	1	2.482			1	5	-1	1.489	1.488	2
0	0	3	2.397	2.398	18	1	3	-4	1.487	1.488	2
0	3	1	2.397			5	2	-4	1.486	1.457	3
1	3	-1	2.383	2.384	3	1	4	3	1.459	1.457	3
4	2	-1	2.378			3	2	-1	1.459	1.439	1
3	2	-2	2.366	2.367	2	5	4	-2	1.453	1.439	1
5	1	-1	2.351			0	0	5	1.438	1.439	1
2	3	0	2.347	2.342	9	1	1	-5	1.437	1.421	6
3	1	2	2.340			3	2	4	1.423	1.421	6
1	1	-3	2.331	2.333	8	3	5	-1	1.420	1.415	6
5	1	0	2.326	2.325	1	4	4	2	1.419	1.415	6
2	1	-3	2.293			8	2	0	1.417	1.415	6
0	1	3	2.287	2.291	22	0	1	5	1.413	1.346	2
2	2	2	2.285			2	4	-2	1.413	1.346	2
2	3	-1	2.284			3	4	3	1.347	1.346	2
3	1	-3	2.183	2.182	14	5	1	-5	1.346	1.346	2
2	3	1	2.181			0	2	5	1.346	1.320	3
1	1	3	2.173	2.165	8	2	1	5	1.320	1.320	3
4	2	1	2.162			2	4	-4	1.320	1.309	2
4	2	-2	2.150	2.149	1	8	3	0	1.309	1.309	2
4	0	2	2.124	2.125	2	0	4	4	1.308	1.294	4
4	0	-3	2.106	2.105	5	1	5	-3	1.293	1.294	4
2	0	3	2.091	2.093	23	0	5	0	1.294	1.273	2
0	3	2	2.076			7	1	3	1.273	1.243	2
5	2	-1	2.074	2.074	2	4	4	-4	1.273	1.243	2
6	0	-1	2.073			2	6	0	1.244	1.215	3
3	2	2	2.066			8	3	-3	1.244	1.215	3
1	2	-3	2.060	2.060	5	9	3	-1	1.217	1.121	2
5	2	0	2.057			2	1	6	1.121	1.121	2
2	3	-2	2.040			11	1	-1	1.120		
6	0	0	2.036	2.037	20						
2	2	-3	2.034								
4	1	-3	2.030	2.030	2						
0	2	3	2.030								

ture to about  $1000^\circ\text{C}$ , using a heating rate of  $10^\circ\text{C min}^{-1}$  and a static air atmosphere (fig. 4).

At temperatures below about  $120^\circ\text{C}$ , the weight-loss curve (labelled TGA) and the temperature-differential curve (labelled DTA) are dominated by events indicating very rapid weight loss and heat absorption respectively. Since lansfordite spontaneously dehydrates to nesquehonite over relatively short times at room temperature, it is not unreasonable to assume that the initial weight loss (amounting to some 34% of the sample weight, or three  $\text{H}_2\text{O}$  molecules) is caused by the conversion of the pentahydrate to the trihydrate, followed by the loss of a third  $\text{H}_2\text{O}$  molecule from the latter (represented by the high-temperature shoulders on the DTA peak at  $90^\circ\text{C}$ ). Support for this suggestion comes from the remarkable similarity between the DTA and TGA events above  $120^\circ\text{C}$  (fig. 4) and those in the corresponding curves measured for nesquehonite by Davies and Bubela (1973). The fourth  $\text{H}_2\text{O}$  molecule in the system is relinquished

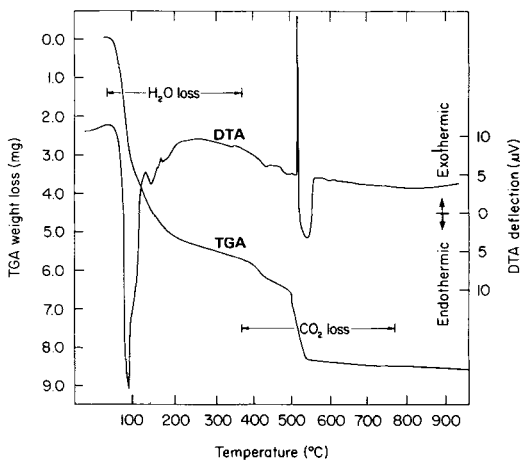


FIG. 4. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves for lansfordite heated at  $10^{\circ}\text{C min}^{-1}$  in static air.

rather more slowly around  $140^{\circ}\text{C}$ , as indicated by a less intense but nevertheless distinct endothermic DTA peak and a gentler TGA slope. The fifth  $\text{H}_2\text{O}$  molecule is released very slowly over the temperature range  $150\text{--}350^{\circ}\text{C}$  and is not accompanied by a major DTA peak. At this stage, about 52% of the original weight has been lost and dehydration is complete.

Decarbonation then follows almost immediately, as indicated by an increase in the TGA slope and an event in the DTA curve. This relatively uniform  $\text{CO}_2$  loss (about 8% by weight) is broken by a

dramatic exothermic peak at  $510^{\circ}\text{C}$ , followed immediately by a strong endothermic peak and a sudden weight loss of some 15%. Similar exothermic peaks around  $500^{\circ}\text{C}$  have been observed during the decarbonation of nesquehonite (Davies and Bubela, 1973), dypingite (Raade, 1970), and hydromagnesite (Sawada *et al.*, 1979) and are interpreted as representing the crystallization of  $\text{MgCO}_3$  from a partially decarbonated amorphous intermediate phase. The rapid evolution of heat accompanying this crystallization decomposes the  $\text{MgCO}_3$  almost immediately and gives rise to an endothermic reaction and rapid  $\text{CO}_2$  loss. The decarbonation process in lansfordite is complete at about  $570^{\circ}\text{C}$ , at which stage some 77% of the original weight has been lost, producing an amorphous mass of  $\text{MgO}$ .

*Infra-red absorption spectrum.* The spectrum shown in fig. 5 was obtained on a Beckman infra-red spectrophotometer, using the double-beam mode and a KBr disc containing about 2 mg of very lightly ground lansfordite. Attempts to improve the quality of the spectrum by using higher and lower lansfordite concentrations (up to 10 mg and down to 0.5 mg) were not successful because of significant degradation in peak resolution and intensity respectively. Moreover, the spectrum obtained when the same lansfordite sample was rerun on a Perkin-Elmer 577 spectrophotometer was essentially identical.

Although the overall distribution of absorption bands for lansfordite is similar to that for other hydrous magnesium carbonates (White, 1974), the peaks are broader and less well defined. This may

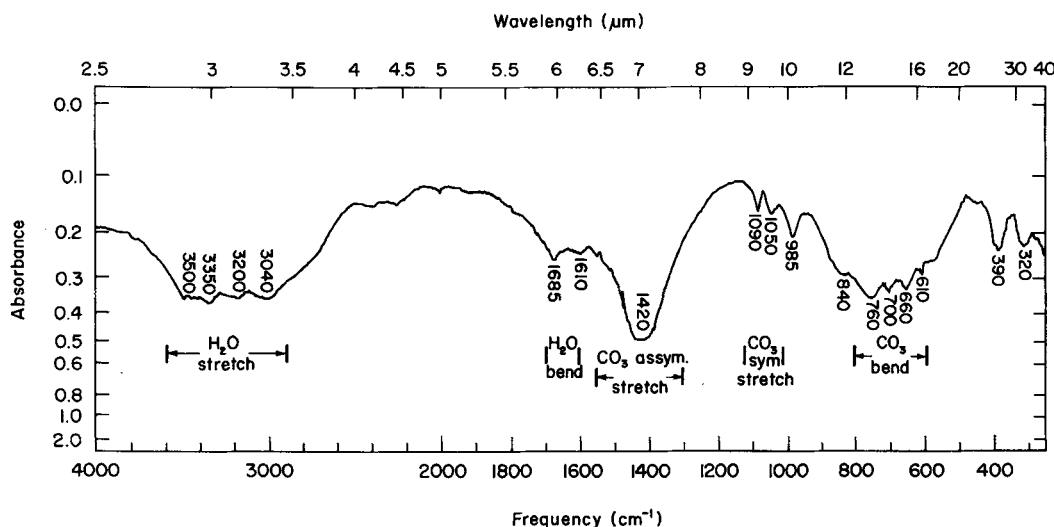


FIG. 5. Infra-red absorption spectrum for lansfordite.

be caused by partial hydration or disordering during preparation or measurement, but an X-ray diffraction pattern of the ground KBr disc did not reveal the presence of any compounds other than KBr and lansfordite.

As shown in fig. 5, the absorption peaks centred around 1420 and 1070  $\text{cm}^{-1}$  can be assigned to  $\text{CO}_3$  asymmetric and symmetric stretching modes respectively, and the broad complex collection of peaks between 600 and 850  $\text{cm}^{-1}$  can be assigned to the appropriate  $\text{CO}_3$  bending modes. The peaks around 1650  $\text{cm}^{-1}$  correspond to the internal bending vibration of  $\text{H}_2\text{O}$ , and the broad, strong band between 2900 and 3600  $\text{cm}^{-1}$  represents  $\text{H}_2\text{O}$  stretching modes shifted from their ideal frequencies to lower values by the effects of hydrogen bonding (Ryskin, 1974). The multiplicity of  $\text{H}_2\text{O}$  absorption bands is to be expected since there are five crystallographically distinct  $\text{H}_2\text{O}$  groups in the unit cell, but the observation of three  $\text{CO}_3$  symmetric stretching peaks implies the presence of at least three distinct  $\text{CO}_3$  groups in the structure. Moreover, the significant amount of line broadening may imply a degree of orientation disorder among the carbonate anions. Detailed interpretation of the infra-red spectrum must therefore await the results of a structure determination for lansfordite.

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#### REFERENCES

- Canterford, J. H., Everson, P. T., and Moyle, F. J. (1981) *Proc. Australas. Inst. Mining Met.* No. 277, 45–52.
- Davies, P. J., and Bubela, B. (1973) *Chem. Geol.* **12**, 289–300.
- Fenoglio, M. (1933) *Period. Mineral.* **4**, 443–62.
- Genth, F. A. (1888) *Z. Kristallogr. Mineral.* **14**, 255.
- Kazakov, A. V., Tikhomirova, M. M., and Plotnikova, V. I. (1959) *Int. Geol. Rev.* **1**, 1–39.
- Langmuir, D. (1965) *J. Geol.* **73**, 730–54.
- Lippmann, F. (1973) *Sedimentary carbonate minerals*. Springer-Verlag, New York, pp. 71–87.
- Palache, C., Berman, H., and Frondel, C. (1951) *Dana's system of mineralogy*, 7th edn., vol. 2, Wiley, New York, pp. 228–30.
- Raade, G. (1970) *Am. Mineral.* **55**, 1457–65.
- Ryskin, Y. I. (1974) In *The infrared spectra of minerals*, Farmer, V. C. (ed.). Monograph 4, The Mineralogical Society, London.
- Sawada, Y., Yamaguchi, J., Sakuri, O., Uematsu, K., Mizutani, N., and Kato, M. (1979) *Thermochim. Acta*, **34**, 233–7.
- Stewart, C. M. (ed.) (1976) *The XRAY system—version of 1976*. Tech. Rep. TR-446, Computer Science Center, University of Maryland.
- White, W. B. (1971) *Am. Mineral.* **56**, 46–53.
- (1974) In *The infrared spectra of minerals*, Farmer, V. C. (ed.). Monograph 4, The Mineralogical Society, London.

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