

SOME ASPECTS OF THE STRUCTURAL RELATIONSHIP
BETWEEN "MESSBACH-TYPE" AND
"LUCIN-TYPE" VARISCITES

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ABSTRACT

A comparative structural study of "Lucin-type" (VL) and "Messbach-type" (VM) variscites by X-ray diffraction and infrared spectroscopy has been performed.

Like "Lucin-type", "Messbach-type" variscite crystallizes in the orthorhombic system, probably with the same space group $Pcab$. The lattice constants found for VM: a , 9.90, b , 9.65, c , 17.18 Å are, however, sufficiently different from those assigned to VL (a , 9.83, b , 9.63, c , 8.55 Å), as to presume the existence of net structural differences. Infrared spectra support this assumption showing the existence of two different types of water molecules, which are present in both structures in different proportion. Some differences in the symmetry of PO_4^{3-} anions between both variscite types were also found.

INTRODUCTION

From X-ray, TDA, TGA, and infrared data of a great number of $AlPO_4 \cdot 2H_2O$ natural samples from several localities, Čech and Slánský (1965, 1968) conclude that such a compound occurs in nature under three modifications: monoclinic metavariscite (syn. "clinovariscite"), orthorhombic variscite (Lucin-type), and variscite Messbach-type (syn. "redondite", "tangeite" and "peganite"). The symmetry of Metavariscite is $P2_1/n$ and its structure has been studied by Borensztajn (1966), Fanfani and Zanazzi (1966), and Moore (1966). Lucin-type variscite symmetry is $Pcab$ (Strunz, 1957) and it is considered isostructural with scorodite ($FeAsO_4 \cdot 2H_2O$), which structure was determined by Kyriyama and Sakurai (1949). The symmetry and unit cell of the latter modification is hitherto unknown, although its X-ray powder pattern and infrared spectrum show a close resemblance to the Lucin-type variscite, suggesting the existence of a close structural relationship between them.

The purpose of the present paper is to investigate the structural differences between both variscite types, in the light of X-ray powder diffraction and infrared spectrum analysis.

MATERIALS

The samples used in this work occur from Palazuelo de las Cuevas, Zamora (Spain). A previous study of this mineral deposit made by Arribas *et al.* (1971), revealed that they are contaminated with metavariscite (15 percent for VL and 7 percent for VM) and with a small quantity of α -quartz. Electron probe microanalysis showed the presence of small quantities of Fe, Cr, Cu, and Ni in substitution for Al (VL sample: Fe 0.26, Cr 0.26, Cu 0.02, Ni 0.03 percent. VM sample: Fe 0.12, Cr 0.08, Cu 0.11, Ni 0.04 percent).

RESULTS AND DISCUSSION

X-ray diffraction

Despite the similarity between VM and VL X-ray patterns, the cell constants obtained by adjusting VL parameters to the VM diffractogram, do not allow a complete indexing¹. After different attempts based on trial and error methods, we concluded that this is only possible by duplicating the unit cell dimensions along *c* axis. Table 1 shows the parameter so obtained. Those corresponding to the VL cell are added for comparison. Indexed VL and VM diagrams are given in Table 2. Contamination of metavariscite (M) and α -quartz (Q) was taken into account for VM diagram.

TABLE 1: UNIT CELL DATA FOR LUCIN AND MESSBACH TYPE VARISCITES

	VL	VM
a (Å)	9.83 ₁	9.90 ₂
b (Å)	9.63 ₅	9.65 ₉
c (Å)	8.55 ₅	17.18 ₀
$a:b:c$	1.020:1:0.888	1.025:1:1.779
Cell. vol. (Å ³)	810.34	1672.99
Sp.g. (Calc)	2.58 ^a	2.50 ^a
Molecules per asym. unit	1	2
Space group	<u>Pcab</u>	<u>Pcab</u>

^aExperimental values go from 2,2 to 2,6 (Palache, Berman and Frondel, 1944).

Because of the VM diagram complexity, assignment of the space group is rather difficult. However, attending to the analysis of the systematic extinctions among isolated reflexions, the *Pcab* space group seems to be probable.

¹From the cell constants so obtained (*a*, 9.898 *b*, 9.663 *c*, 8.589 Å), reflections corresponding to 3.74, 2.45, 2.21, 2.18, 2.01, and 1.78 Å interplanar spacings cannot be indexed.

TABLE 2. INDEXED X-RAY POWDER DIFFRACTOGRAMS FOR LUCIN AND MESSBACH TYPE VARISCITES.

VM				VL			
h k l	dcal	dobs	Ir	h k l	dcal	dobs	Ir
0 1 2	6.419			1 1 1	5.358	5.356	72
1 1 1	6.413	6.408	8	2 0 0	4.908	4.904	6
	M	6.32	3	0 2 0	4.810	4.810	30
1 1 2	5.385	5.387	61	0 0 2	4.280	4.26	65
0 2 0	4.831	4.831	47	2 0 1	4.257		
2 0 1	4.755	4.753	5	0 1 2	3.910	3.904	28
	M	4.54	3	2 1 1	3.893		
1 1 3	4.410	4.407	47	1 2 1	3.856	3.856	4
2 1 0	4.404			1 1 2	3.632	3.633	18
0 0 4	4.294			2 2 0	3.435	3.437	2
2 0 2	4.288	4.290	100	2 0 2	3.225	3.226	8
	M	4.23	4	0 2 2	3.197	3.192	8
0 1 4	3.924	3.920	27	2 2 1	3.188		
2 1 2	3.918			1 2 2	3.040	3.041	100
1 2 2	3.874	3.872	4	3 1 1	2.913	2.914	43
2 0 3	3.743	3.742	15	1 3 1	2.871	2.873	39
1 1 4	3.647	3.650	11	3 2 0	2.705	2.703	26
2 1 3	3.491	3.490	5	1 1 3	2.635	2.635	14
1 2 3	3.459	3.459	31	3 2 1	2.579	2.580	8
2 2 0	3.455	3.34	6	0 3 2	2.566	2.567	6
	Q	3.208	10	2 3 1	2.561		
0 2 4	3.210			1 3 2	2.483	2.483	22
2 2 2	3.204			2 0 3	2.466	2.467	7
1 1 5	3.076			4 0 0	2.454	2.455	16
2 1 4	3.073	3.075	4	2 1 3	2.389	2.389	4
3 1 1	3.070			1 2 3	2.381	2.381	2
1 2 4	3.052	3.054	41	4 0 1	2.359	2.360	1
3 1 2	2.933	2.935	14	1 4 0	2.336	2.336	12
1 3 2	2.884	2.885	23	4 1 1	2.291	2.290	5
3 1 3	2.740	2.740	31	3 3 2	2.287		
1 3 3	2.699	2.700	45	2 3 2	2.274	2.275	4
2 3 0	2.698			3 3 1	2.212	2.213	2
1 2 5	2.693	2.693	8	2 2 3	2.195	2.197	2
2 2 4	2.692			2 4 0	2.160	2.160	3
1 1 6	2.644	2.645	7	0 0 4	2.140	2.139	5
3 2 2	2.597	2.597	4	4 2 1	2.118	2.119	3
0 3 4	2.576			3 1 3	2.098	2.098	2
2 3 2	2.573	2.575	9	0 4 2	2.097		
1 3 4	2.493	2.493	10	2 4 1	2.094	2.094	4
2 0 6	2.478			1 3 3	2.083	2.084	12
4 0 0	2.472	2.475	18	1 4 2	2.050	2.051	4
4 0 1	2.448	2.449	5	3 3 2	2.019	2.020	5
0 4 0	2.415	2.415	3	3 2 3	1.963	1.960	5
2 1 6	2.399	2.400	9	2 0 4	1.961		
0 3 5	2.349	2.347	5	2 3 3	1.955	1.955	5
1 4 0	2.345			0 2 4	1.955		
0 4 2	2.325	2.325	11	4 2 2	1.947	1.947	8
1 4 1	2.324			2 4 2	1.928	1.928	2
1 1 7	2.312	2.312	7	2 1 4	1.922	1.921	5
3 1 5	2.310			1 2 4	1.917	1.917	8
1 3 5	2.286			4 3 1	1.900	1.900	2
2 3 4	2.283	2.285	4	5 1 1	1.877	1.876	1
3 3 1	2.283			4 0 3	1.860	1.860	8

h	k	l	dcal	dobs	Ir	h	k	l	dcal	dobs	Ir
0	4	3	2.225	2.225	2	1	5	1	1.844	1.843	4
3	3	2	2.225			4	1	3	1.827	1.827	1
4	1	3	2.209	2.210	3	5	2	0	1.817		
2	2	6	2.203			2	2	4	1.816	1.816	1
4	2	0	M 2.197	2.200	3	1	4	3	1.807	1.807	2
2	0	7	2.197			3	3	3	1.786	1.786	2
1	4	3	2.171			0	3	4	1.780		
2	4	0	2.170	2.170	1	5	2	1	1.778	1.779	2
0	0	8	M 2.147	2.147	5	0	5	2	1.755	1.754	12
1	2	7	2.136			5	1	2	1.754		
3	3	3	2.136	2.137	4	1	3	4	1.751	1.751	10
2	3	5	2.121	2.122	2	2	4	3	1.722	1.722	4
0	4	4	2.105	2.106	6	4	4	0	1.718	1.718	5
1	3	6	2.090	2.091	5	3	2	4	1.678	1.678	2
1	4	4	M 2.058	2.059	2	2	3	4	1.673		
2	4	3	2.029			5	2	2	1.673	1.673	3
3	3	4	2.029	2.030	6	5	3	1	1.643	1.643	1
4	0	5	2.005	2.007	3	3	5	1	1.628	1.628	1
3	0	7	1.968			4	3	3	1.609		
2	0	8	1.968	1.969	1	6	0	1	1.607	1.608	5
4	2	0	1.959			0	6	0	1.603		
4	3	0	1.959	1.959	9	3	4	3	1.603	1.604	8
0	3	7	1.952			1	2	5	1.591		
3	4	0	M 1.947	1.950	4	4	1	4	1.591	1.590	9
4	3	1	1.947			1	4	4	1.578	1.578	6
1	2	8	1.924			3	3	4	1.563	1.563	3
5	1	1	1.923	1.924	1	5	3	2	1.559	1.559	6
1	3	7	1.915			4	2	4	1.529		
3	3	5	1.913	1.914	5	6	0	2	1.528	1.528	3
3	4	2	1.898			2	6	0	1.524		
1	5	0	1.897	1.896	1	6	2	1	1.524	1.524	3
5	1	2	1.886			2	5	3	1.517	1.517	12
0	5	2	1.885	1.885	1	0	6	2	1.501		
1	5	1	1.884			2	6	1	1.500	1.500	4
1	0	9	1.874			3	1	5	1.498		
0	1	9	1.872	1.872	1	5	4	1	1.497	1.498	4
4	0	6	1.871			3	2	5	1.447	1.446	8
1	5	2	1.851	1.852	4	0	5	4	1.431		
1	1	9	1.839	1.839	1	5	1	4	1.430	1.431	4
4	1	6	1.837	1.837	2	4	5	2	1.427		
3	2	7	1.822			0	0	6	1.427	1.427	3
2	2	8	1.822	1.823	1	0	1	6	1.411	1.411	2
2	3	7	M 1.816	1.815	1	6	1	3	1.404		
1	4	6	1.814			4	0	5	1.404	1.404	4
1	5	3	1.799			1	1	6	1.397	1.396	1
2	5	0	1.797	1.798	1	2	0	6	1.370	1.370	3
3	0	8	1.797			7	1	1	1.370		
3	3	6	1.794			5	5	1	1.357	1.357	1
5	0	4	1.794	1.792	1	6	4	0	1.353	1.353	1
5	2	2	1.788			4	6	0	1.342		
2	5	1	1.788	1.787	1	5	4	3	1.342	1.342	5
0	3	8	1.786			6	4	1	1.336	1.336	1
4	3	4	M 1.782	1.781	1	4	6	1	1.326	1.326	1
2	0	9	1.781			2	2	6	1.317	1.317	1
3	1	8	1.767	1.768	1	3	5	4	1.311	1.311	1
0	5	4	M 1.762	1.761	2	1	7	2	1.297	1.297	1
2	5	2	1.761			6	1	4	1.288	1.288	1

VM

VL

Philips PW-1051 diffractometer with proportional counter Cu K_α radiation, and 1°/0, 1°/1° divergence, receiving and scatter slits used. Goniometer speed 1/8°/min; chart speed 40 cm/h. Powder samples analysed using a rotating sample holder. (200) reflection of NaCl (*d* = 2, 8195 Å) used as standard.

Infrared Spectra

Figure 1 shows infrared spectra of both variscite types between 400 and 4000 cm^{-1} . The spectra of a pure synthetic metavariscite have been included for comparison. The wave numbers (cm^{-1}) of the most significant bands are given.

The differences in resolution of the spectra are due to the different degree of crystallinity of the samples. Powder diffractograms and petrographic microscopy observations indicate that VL sample is more crystalline than VM.

In OH stretching vibration region (2500 to 4000 cm^{-1}), the spectra are very similar. The most significant differences between them are in the relative intensities of their bands, especially for those at 3580 and 3100 cm^{-1} .

The bands of this region indicate the existence of hydrogen bonds of different energy. By considering a linear relationship between distances and infrared stretching frequencies in O—H—O bridges, and taking into account the data of Pimentel and Sederholm (1956), together with the obtained from the metavariscite's structure (Borensztajn, 1966), the observed frequencies indicate variations in O—H—O distances from 2,55 Å (2920 cm^{-1}) to 2.70 Å (3340 cm^{-1}). The sharp band at 3580 cm^{-1} represents a distance too long (2,9 Å) to denote the existence of an hydrogen bridge.

In the water deformation region both samples present two wide bands at about 1630 and 1570 cm^{-1} , indicating the existence of two different types of water molecules W_1 and W_2 ¹. If it is assumed that the lowest bending frequency band (1570, 1555 cm^{-1}) is associated together with the highest stretching one (3580 cm^{-1}) to the same water molecules W_2 , these molecules must possess at least one of its two hydrogen atoms not bonded to the structure. On the other hand, W_1 type (associated to the 1630, 1635 cm^{-1} frequencies) would be bonded to the structure through its two hydrogen atoms.

The relative intensity of the bands at 3580 and near 1570 cm^{-1} is lower in VM than in VL spectrum. This must be a consequence of the lower proportion of W_2 water type in the VM structure. Considering the existence of two independent water molecules per asymmetric unit in VL and four in VM (Table 1), the water proportion $W_1:W_2$ should be 1:1 for "Lucin" variscite against 3:1 for "Messbach" variscite.

P—O stretching and bending vibration contribute bands from 1200

¹Two endothermic effects about 185 and 225°C in their TDA diagrams (Arribas *et al.*, 1971), favor this conclusion.

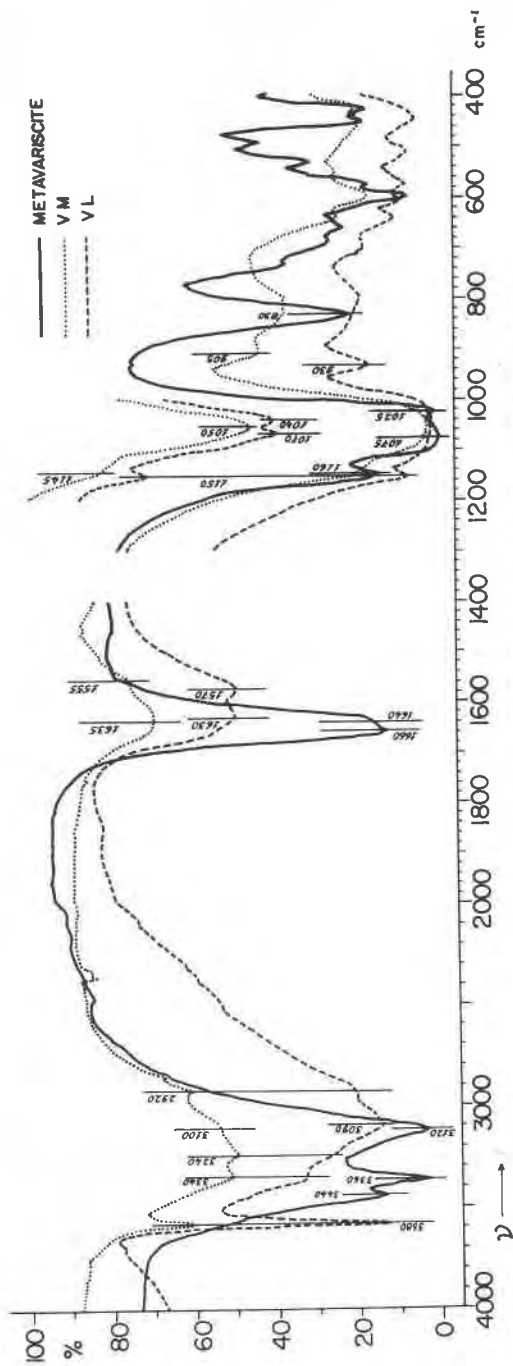


Fig. 1. Infrared spectra of Lucin and Messbach type variscites and metavariscite.

Spectra obtained with a Perkin Elmer 225 spectrophotometer. Samples kept for several weeks in a desiccator in presence of silica gel to avoid the presence of extraneous water. Fluorolube mulls used as absorption cells. KBr discs employed in P-O vibration region (400 to 1200 cm^{-1}).

to 400 cm^{-1} , which interfere with those due to rotation and translation movements of water molecules; therefore, a complete assignment in this region proves difficult. Adler (1964, 1968), studying the P—O vibrations on PO_4^{3-} group of natural phosphates, emphasizes the influence of the group symmetry on the number of infrared-active modes. Table 3 shows such a correspondance. According to this scheme both samples present differences in the symmetry of their PO_4^{3-} groups. In fact, while VM spectrum present only two bands at 1145 and 1050 cm^{-1} , assignable to the ν_3 mode, VL shows three absorptions at 1150, 1070, and 1040 cm^{-1} . On the other hand, the existence of one unique band at 905 cm^{-1} in VM spectrum, assignable to the ν_1 mode, shows that one at least of the two independent PO_4^{3-} anions of the asymmetric unit must possess C_{3v} symmetry. Through a similar reasoning, it may be seen that the unique PO_4^{3-} anion of the asymmetric unit in VL structure must possess either C_{2v} or C_s symmetry.¹

The absence of bands near 2600 cm^{-1} (P-OH vibrational region), shows, in agreement with Arlidge *et al.* (1963), that OH structural groups are absent in both structures.

TABLE 3: POSSIBLE MOLECULAR POINT GROUPS AND VIBRATION MODES FOR THE PO_4^{3-} ION, WHERE P IS ON A \underline{C}_B SITE (FROM ADLER, 1964)

Molecular Point Group	Number of Infrared Active Vibrations			
	ν_3	ν_1	ν_4	ν_2
\underline{T}_d	1	0	1	0
\underline{D}_{2d}	2	0	2	0
\underline{C}_{3v}^a	2	1	2	1
\underline{C}_{2v}^a	3	1	3	1
\underline{C}_s^a	3	1	3	2

^aPoint groups to which a molecule with a dipole moment might belong.

CONCLUSIONS

Powder X-ray diffraction results seem to indicate that "Messbach-type" variscite, like "Lucin-type", is orthorhombic with space group $Pcab$. However, the small difference between their X-ray patterns

¹Since ν_4 vibration modes do not provide additional information, a more precise assignment is not possible in the absence of data about ν_2 vibrations modes.

involve a change in the unit cell dimensions. Accepting that the VM cell possesses doubled length along the c axis, conserving VL specific gravity, a close structural relationship can be expected between both variscites. Thus, the VL cell might be considered as a VM pseudocell in which both two independent molecules belonging to the asymmetric unit become equivalents. Laueite and Stewartite is an analogous case of polymorphic phosphates $[\text{MnFe}_2(\text{OH})_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$, in which the structure of the former is a substructure of the second with period $a/2$ (Peacor, 1963).

Infrared spectra support the above conclusions showing net differences between both samples: there are two types of water molecules W_1 and W_2 . W_1 possesses its two hydrogen atoms bonded to the structure through O—H—O bridges from 2.55 to 2.70 Å, while W_2 only possess one of them bonded to the structure, the other one being free. The $W_1:W_2$ proportion is 1:1 for VL against 3:1 for VM. No O—H structural groups are present in both structures. The symmetry of the PO_4^{3-} anion in the VL structure is different from VM.

Summarizing, the results herein seem to confirm the existence of two polymorphic variscite species, "Messbach" and "Lucin" types, closely structurally related. The known fact that "Messbach-type" variscite always occurs in form of cryptocrystalline aggregates, the only single crystals so being of "Lucin-type" (often coexisting with a cryptocrystalline mass of VM), suggests that "Messbach-type" variscite is a metastable crystalline state of the orthorhombic $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$, formed under natural conditions which do not allow a greater structural order.

ACKNOWLEDGMENTS

We thank Dr. J. M. Serratosa for help in the interpretation of the infrared spectra and the critical review of the respective part in the manuscript.

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Manuscript received, December 31, 1970; accepted for publication, September 21, 1971.