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Crystal structure of coalingite

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SUMMARY. The crystal structure of coalingite ($Mg_{10}Fe_2(OH)_{24}(CO_3).2H_2O$) has been determined using single-crystal X-ray methods. The mineral is trigonal, with space group $R\bar{3}m$, $a_H = 3{\cdot}12$, $c_H = 37{\cdot}4$ Å, $Z = \frac{1}{2}$, and (0001) cleavage. The structure is of a layer type, and is based on a structural element about 12·5 Å thick in the c-direction and consisting of two brucite-like layers and one disordered layer containing carbonate ions and water molecules and resembling those in sjögrenite and pyroaurite. The unit cell comprises three of these structural elements stacked together in the c-direction. The Mg^{2+} and Fe^{3+} ions are randomly distributed among all the octahedral sites of the brucite-like layers. The structure closely resembles those of sjögrenite and pyroaurite, but has two brucite-like layers between each CO_3^{2-}–H_2O layer where these have one. There is a tendency to random interstratification, and the crystals appear to contain intergrown regions of brucite and of sjögrenite or pyroaurite. Coalingite-K probably has a similar structure, but with three brucite-like layers between each CO_3^{2-}–H_2O layer; its idealized formula is probably

$$Mg_{16}Fe_2(OH)_{36}(CO_3).2H_2O.$$

COALINGITE forms platey crystals and has the approximate composition $Mg_{10}Fe_2(OH)_{24}(CO_3).2H_2O$. It resembles brucite, pyroaurite, and similar minerals, but is clearly distinguished from all of these by its X-ray powder pattern. It was first found in the New Idria serpentinite at Coalinga, California, by Mumpton, Jaffe, and Thompson (1965); Jambor (1969) reported a second occurrence in the Muskox Intrusion, Canada. The above formula relates to the Coalinga specimen; Jambor (1969) found a slightly different composition and considered that appreciable variation was possible.

The previous investigations included chemical analyses, optical, X-ray powder, infra-red absorption, and thermal decomposition studies and specific gravity determinations. In both cases, X-ray single-crystal investigation was attempted but gave only limited information because of the poorness of the material. Mumpton, Jaffe, and Thompson (1965) concluded that the mineral was possibly hexagonal and that it might be a faulted single phase or an intimate mixture of two phases having the same orientation. Jambor (1969) concluded that it was trigonal, with $a = 3{\cdot}1$ Å and $c \geqslant 30$ Å. No attempts to solve the crystal structure were made.

Mumpton, Jaffe, and Thompson (1965) also described a second mineral, which they called coalingite-K. This closely resembled coalingite, but had a significantly different X-ray powder pattern and differed slightly from it in specific gravity and optical properties. Because of the small quantity available, they made no chemical analysis, but considered that the mineral might be a compositional variation of coalingite. Through the kindness of Prof. Mumpton, specimens of coalingite and coalingite-K were made available to us for further examination. Both consisted of reddish-brown platelets conforming to the original description.

Experimental methods and crystal data

Oscillation, rotation, and Weissenberg photographs about *a* showed that coalingite is trigonal, with space group $R\bar{3}m$, $R3m$, or $R32$, and $a = 3{\cdot}12$, $c = 37{\cdot}4$ Å ($V = 315{\cdot}3$ Å^3), referred to hexagonal axes. These cell parameters are values slightly refined by indexing the powder pattern given by Mumpton, Jaffe, and Thompson (1965). The subsequent structure determination showed the space group to be $R\bar{3}m$. If the cell contents are taken as $\frac{1}{2}[Mg_{10}Fe_2(OH)_{24}(CO_3).2H_2O]$ referred to the hexagonal cell, the X-ray density is 2·26 g.cm^{-3}; the observed density (Mumpton, Jaffe, and Thompson, 1965) is 2·32–2·33 g.cm^{-3}. The crystals are irregularly shaped plates with (0001) cleavage.

All the crystals examined were twinned by reflection across (0001), though not always with equal proportions of the two components. The X-ray reflections always showed marked angular spread; in addition, some were broadened or diffuse, and in some regions of reciprocal space they were streaked along lines parallel to c^*, indicating stacking disorder. The combination of these effects made indexing difficult, though only rarely uncertain. There were a few, weak reflections that could not be indexed, and which were possibly attributable to brucite together with pyroaurite or sjögrenite, all in the same orientation as the coalingite. This result confirms Mumpton, Jaffe, and Thompson's (1965) suspicion that another phase might be present in parallel orientation. The 0003 coalingite reflection was markedly abnormal; there was a streak of moderate intensity extending along the c^*-axis over the approximate range 7 to 24 Å, with a maximum at about 13·5 Å. This is significantly displaced from the theoretical spacing of 12·5 Å.

For intensity measurements, a crystal of approximate size 0·15×0·15×0·03 mm was mounted about *a*. It contained the two twin orientations in a ratio of about 2·7:1. An attempt to measure intensities using an automatic linear diffractometer failed because of the unfavourable shape of the X-ray reflections, and measurements were therefore made by visual estimation using the multiple-film Weissenberg method with filtered copper radiation. They were highly approximate, and it was evident that it would be possible only to determine the broad features of the structure. Absorption corrections were applied using Albrecht's (1939) method.

Determination of the structure

A trial structure was derived by analogy with the structures of sjögrenite and pyroaurite (Allmann and Lohse, 1966; Ingram and Taylor, 1967; Allmann, 1968). In these structures, brucite-like layers alternate with disordered intermediate layers containing CO_3^{2-} ions and H_2O molecules (fig. 1, A). The cation sites in the brucite layers are occupied by Mg^{2+} and Fe^{3+}, which are often distributed randomly, though crystals, or regions of crystals, in which the cations are ordered also occur (Taylor, 1969). Sjögrenite is the 2*H*-polytype, in which the unit cell contains two of the elementary units shown in fig. 1, A in the *c*-direction, while pyroaurite is the 3*R*-

polytype. The chemical composition, unit-cell parameters, and atomic cell contents of coalingite strongly suggest a structure resembling those of sjögrenite and pyroaurite, but with two brucite-like layers between each carbonate and water layer instead of one (fig. 1, B). The rhombohedral lattice and *c*-axial length of coalingite could be explained by assuming it to be the 3*R*-polytype, with three of the units shown in fig. 1, B per unit cell.

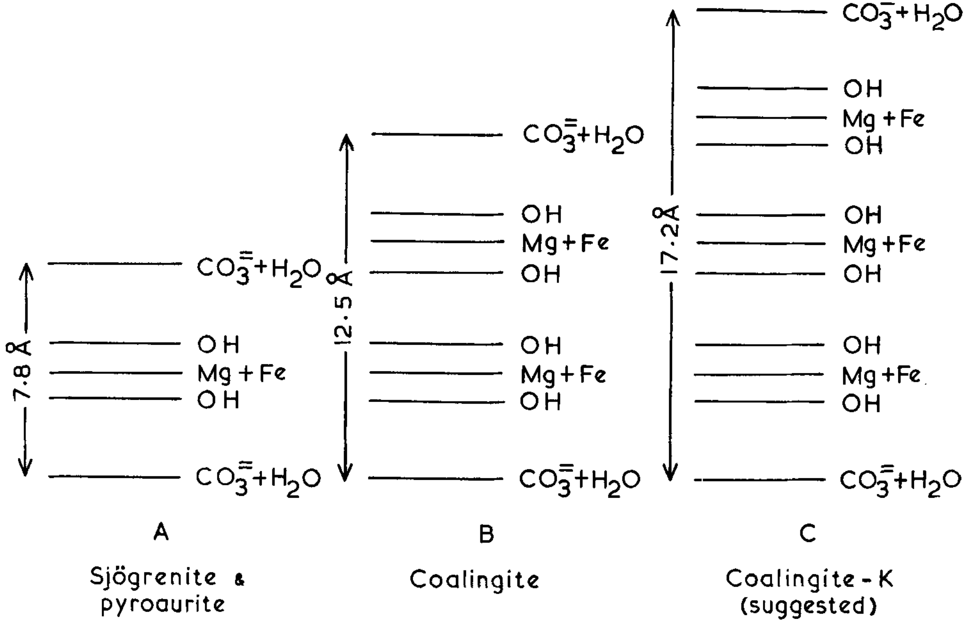

FIG. 1. Layer sequences in (A) sjögrenite and pyroaurite, (B) coalingite, and (C) coalingite-K (suggested). The thicknesses in the *c*-direction of the structural elements are shown in each case.

In deriving the detailed trial structure, the following assumptions were made. The Mg^{2+} and Fe^{3+} were assumed to be completely disordered among all the octahedral sites. The two brucite-like layers in each pair were assumed to pack together as in brucite, with the metal cations of the two layers coinciding in *ab*-projection and the hydroxyl groups on the lower surface of one layer fitting into the hollows between three hydroxyl groups on the upper surface of the next. Each intermediate or CO_3–H_2O layer was assumed to contain oxygen sites arranged in closely spaced groups of six, as suggested by Ingram and Taylor (1967) for the intermediate layer in pyroaurite, assuming the latter to have space group $R\bar{3}m$ (fig. 2, A). In each such group of six sites, not more than one can be occupied by an oxygen atom, which may form part, either of a water molecule, or of a carbonate group; in each intermediate layer there is one of these groups of sites to the cross-section of the unit cell. It was assumed that the CO_3^{2-} ions and H_2O molecules were distributed at random. If the chemical formula is taken into consideration, these considerations lead to a statistical occupancy of

5/36 oxygen atom per interlayer site, one group of sites in six being entirely unoccupied. The carbon atoms, which must also be statistically distributed, were omitted. Lastly, it was assumed that the relative positions of the groups of interlayer oxygen sites and the hydroxyl groups of the brucite layers on either side of them were the same as in pyroaurite. Fig. 2, A shows the postulated structure of the intermediate layer in plan, with typical situations for CO_3^{2-} groups and H_2O molecules indicated, and fig. 2, B shows the relationships between the sites in the intermediate layer and the hydroxyl ions of the adjacent brucite layers. The hydroxyl ions coincide in *ab*-projection; that is, if the existence of the intermediate layer is ignored, the brucite layers pack together at these points in the structure as in gibbsite and not as in brucite.

It was found possible to construct a trial structure satisfying these assumptions, and having the space group $R\bar{3}m$, and this is shown in fig. 3. The interatomic distances were adjusted to give reasonable values, taking into account the observed Mg:Fe ratio. A preliminary structure factor calculation gave $r \approx 0{\cdot}4$ on all reflections. It was observed that, within lines in reciprocal space of constant h and k, the agreement was very much better than this result would indicate and it was concluded that the proposed structure was essentially correct but that, owing to the considerable difficulties in determining the intensities, the application of individual scale factors to these lines was justified. This was done and a few cycles of block-diagonal least squares refinement were applied to improve the z-coordinates and isotropic temperature factors of the atoms. This reduced the r-factor to 0·19 on all reflections; it was considered that the limitations imposed by the data had been reached, and no attempt was made to refine the structure further. Table I gives observed and calculated structure factors, table II the final parameters, together with the most important interatomic distances and angles. These show no unexpected features; to within experimental error, the two sets of cation-oxygen distances in the octahedral layers are equal, at 2·09±0·02 Å.

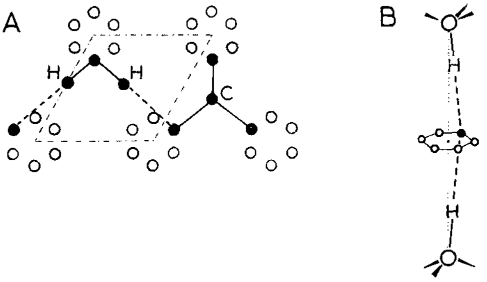

FIG. 2. The intermediate layer of CO_3^{2-} ions and H_2O molecules. A: Plan view showing arrangement of oxygen sites. Not more than one site in each group of six can be occupied; typical situations of CO_3^{2-} ions (right) and H_2O molecules (left) are shown, including in the latter case the intra-layer hydrogen bonds on to adjacent oxygen atoms. All circles represent oxygen sites unless otherwise indicated. Dot-dash lines outline the unit cell (a = 3·12 Å). B: Spatial relationship between any of the groups of six sites in the intermediate layer and the hydroxyl groups of the brucite-like layers above and below it. Hydrogen bonds from the latter to the one occupied site in the intermediate layer are shown.

As a final check on the proposed structure, a three-dimensional difference map was computed. It showed values that were almost everywhere within the range ±2·0 eÅ^{-3}, the largest deviations being approximately in the places expected for the hydrogen atoms of the hydroxyl groups (fig. 2, B), which gave peaks of +3·0 eÅ^{-3}. These results support the proposed structure.

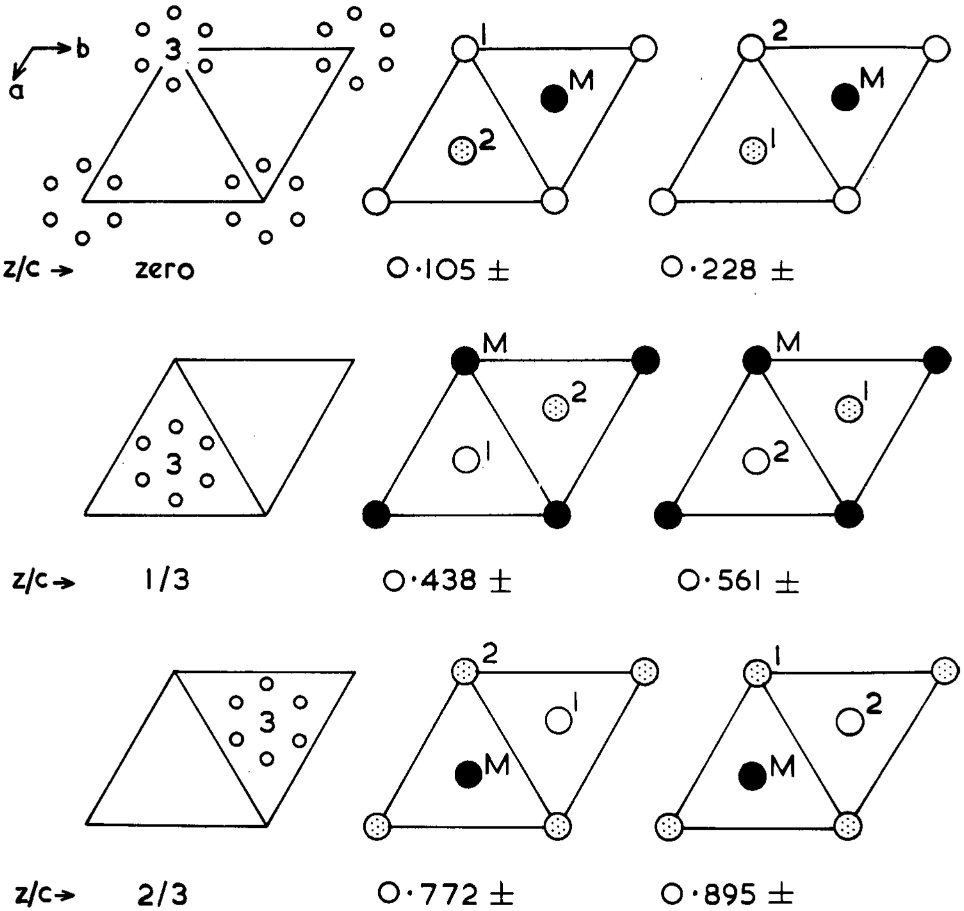

FIG. 3. Crystal structure of coalingite, shown as nine sections or slices of the unit cell at different heights up the *c*-axis. The sections at zero, ⅓, and ⅔ are the carbonate–water layers; small circles labelled 3 represent the oxygen sites, each of which has a statistical occupancy of 0·14. Carbon and hydrogen sites are not shown. The other slices represent the brucite-like layers; their heights are given in the form $Z\pm$, where Z is the coordinate of the metal cation and the ± indicates that hydroxyl ions occur above and below this. The metal cations are shown as full circles and marked M. Hydroxyl ions below and above the metal cations are shown as open and shaded circles respectively; the figure 1 or 2 indicates the set of oxygen sites to which each belongs.

X-Ray powder pattern

Table III gives the X-ray powder data reported by Mumpton, Jaffe, and Thompson (1965), and spacings and intensities calculated for the structure described here. Powder data reported by Jambor (1969) agree substantially with those of Mumpton, Jaffe, and Thompson (1965). The calculated intensities, which were placed on an arbitrary scale to facilitate comparison with the observed values, are based on the F_c values given in table I; copper radiation and Debye-Scherrer (or diffractometer)

TABLE I. *Coalingite: observed and calculated structure factors*

hk	*l*	$\|F_o\|$	F_c	*hk*	*l*	$\|F_o\|$	F_c	*hk*	*l*	$\|F_o\|$	F_c	*hk*	*l*	$\|F_o\|$	F_c
00	3	*	−39	01	−7	9	14	02	−8	64	−62	03	−9	25	29
	6	51	−60		8	114	−96		10	17	−20	11	0	86	83
	9	90	80		−10	8	−9		−11	19	24		3	26	−32
	12	11	8		11	41	48		13	17	−17		6	42	−41
	15	20	3		−13	19	−12		−14	40	39		9	45	48
	18	12	22		14	59	71		16	50	45		12	15	−6
	21	19	15		−16	79	68		−17	46	−50	12	−1	26	−29
	24	24	−31		17	74	−68		19	13	−18		2	26	20
	27	15	23		−19	17	−22		−20	10	6		−4	12	0
	30	44	43		20	24	12		22	29	−35		5	16	17
	33	50	−47		−22	49	−48		−23	23	27		−7	12	22
	36	11	6		23	45	36		25	43	44		8	63	−45
	39	35	39		−25	74	66	03	0	36	39		−10	15	−19
	42	17	−27	02	1	36	−32		3	10	−17		11	17	16
01	−1	15	−16		−2	28	26		−3	10	−17		−13	13	−15
	2	48	44		4	15	1		6	25	−23		14	47	27
	−4	18	10		−5	17	24		−6	25	−23		−16	35	34
	5	33	42		7	11	22		9	25	29		17	50	−38

* Unmeasurable; see text.

TABLE II. *Coalingite: atomic parameters, interatomic distances, and angles. Coordinates are given as fractions, referred to the hexagonal axes. Estimated standard deviations on last significant digit in parentheses*

Atom	Site Symmetry	Site Multiplicity	*x/a*	*y/b*	*z/c*	*B* (Å²)	Occupancy
Mg, Fe	3*m*	6	$\frac{1}{3}$	$\frac{2}{3}$	0·1047(3)	0·0(1)	0·87 Mg+0·17 Fe
O(1)	3*m*	6	0	0	0·076(1)	6·1(10)	1·00 O
O(2)	3*m*	6	$\frac{2}{3}$	$\frac{1}{3}$	0·132(1)	2·5(7)	1·00 O
O(3)	*m*	18	0·105	0·210	0	3·0(20)	0·14 O

In (Mg,Fe)(OH)$_6$ octahedra				Between layers	
Distances		Angles		Distances	
(Mg, Fe)—O(1)	2·10(3) Å	O(1)—(Mg, Fe)—O(1)	96°(1)	O(1)—O(3)	2·89(6) Å
(Mg, Fe)—O(2)	2·07(2)	O(1)—(Mg, Fe)—O(2)	83°(1)	O(2)—O(2)	3·15(5)
O(1)—O(1)	3·12	O(2)—(Mg, Fe)—O(2)	98°(1)		
O(1)—O(2)	2·77(6)				
O(2)—O(2)	3·12				

geometry were assumed, and no absorption corrections were introduced. In general the agreement between the observed and calculated patterns, as regards both spacings and intensities, is as good as could be expected in view of the broadening and streaking of the reflections in the single-crystal photographs, and provides further evidence for the essential correctness of the proposed structure.

The 4·75 Å spacing reported by Mumpton, Jaffe, and Thompson (1965) was visible as a basal reflection on Weissenberg photographs, and is probably due to intergrown brucite (d_{0001} for pure $Mg(OH)_2 = 4{\cdot}77$ Å). The spacings and intensities of the 13·4 Å reflection, and to a smaller extent the 6·05 Å reflection, agree poorly with the calculated values. This is compatible with the single-crystal evidence, and its significance is discussed later.

TABLE III. *Coalingite: X-ray powder data*

Calculated*			Observed†		Calculated			Observed	
hkl	*d*	I_{rel}	*d*	I_{rel}	*hkl*	*d*	I_{rel}	*d*	I_{rel}
003	12·47 Å	200	13·4 Å	40B	1.0.19	1·591 Å	2	—	—
006	6·23	99	6·05	50	110	1·560	28	1·558 Å	50
—	—	—	4·75	10‡	0.0.24	1·558	1	—	—
009	4·16	79	4·20	80	113	1·548	8	—	—
0.0.12	3·12	<1	—	—	0.1.20	1·538	<1	—	—
101	2·70	4	—	—	116	1·513	13	1·509	10
012	2·67	29	2·67	30	119	1·461	16	1·462	10
104	2·60	1	2·62	5	1.0.22	1·439	8	1·430	5
015	2·54	23	2·52	10B	1.1.12	1·395	<1	—	—
0.0.15	2·49	<1	—	—	0.1.23	1·393	4	—	—
107	2·41	2	—	—	0.0.27	1·385	<1	—	—
018	2·34	105	2·34	100	021	1·350	3	—	—
1.0.10	2·19	<1	—	—	202	1·348	2	—	—
0.1.11	2·12	20	§	§	024	1·337	<1	—	—
0.0.18	2·08	1	—	—	205	1·330	2	—	—
1.0.13	1·970	1	—	—	1.1.15	1·323	4	—	—
0.1.14	1·900	33	1·884	30	027	1·310	1	—	—
0.0.21	1·781	<1	—	—	1.0.25	1·309	11	1·313	5
1.0.16	1·768	25	1·767	30	208	1·298	8	1·298	10
0.1.17	1·706	23	1·712	30					

* This investigation. Intensities assume copper radiation and Debye-Scherrer geometry. Spacings assume cell parameters $a = 3{\cdot}12$, $c = 37{\cdot}4$ Å, space group $R\bar{3}m$.

† Coalingite from type locality; data of Mumpton, Jaffe, and Thompson (1965).

‡ Probably due to intergrown brucite.

§ 2·14 Å spacing of relative intensity <5 on the above scale is reported by Jambor (1969) for the Muskox specimen.

Discussion

The close similarities between coalingite and sjögrenite or pyroaurite in such respects as infra-red absorption spectra and thermal decomposition behaviour (Mumpton, Jaffe, and Thompson, 1965; Jambor, 1969; Rouxhet and Taylor, 1969) are readily explained by the structural relationship found in the present work. Coalingite has a lower ratio of iron to magnesium than have typical specimens of sjögrenite or pyroaurite, which have compositions around $Mg_6Fe_2(OH)_{16}(CO_3).4H_2O$. It might, therefore, seem reasonable to suppose that on oxidation and carbonation, iron-rich brucites would give sjögrenite or pyroaurite, and that ones lower in iron would give coalingite. However, there is probably some overlap in ranges of composition, since some sjögrenites contain regions in which the Mg:Fe ratio appears to be 12:1 or even higher (Taylor, 1969). The conditions under which coalingite is formed in preference to sjögrenite or pyroaurite are thus not clear, and further synthetic work would be desirable to clarify this question.

The crystal structure found in the present work is an idealized one. The streaking and broadening of the X-ray reflections shows that irregularities in the layer stacking occur. These probably affect more than the stacking of the structural elements; the sequence of two brucite-like layers and one carbonate–water layer is probably not rigidly followed, so that regions approximating on the one hand to brucite and on the other to sjögrenite or pyroaurite may occur. Where such regions are large enough to diffract independently, they will give rise to the X-ray reflections of the appropriate phase, but where they are smaller, effects typical of randomly interstratified structures will be observed. The anomalous 13·4 Å and 6·05 Å basal reflections can probably be explained in this way.

Jambor (1969) interpreted the chemical analysis of the Muskox specimen as indicating a formula $Mg_{8\cdot31}Fe_2(CO_3)_{0\cdot38}(OH)_{22\cdot06}H_{1\cdot35}O_{1\cdot51}$. This does not balance; the interpretation of the analysis can also be criticized in that part of the ignition loss (about 4 % on the initial weight of material) was attributed to adsorbed organic liquid used for purification. It seems more likely that virtually all of the total ignition loss of 33·4 % was due to H_2O and CO_2. The results are more rationally explained if the formula is written as $[(Mg_{9\cdot4}Mn_{0\cdot2}Fe^{2+}_{0\cdot1}Fe^{3+}_{2\cdot3})(OH)_{24}](CO_3)_{0\cdot32}(OH)_{1\cdot66}(H_2O)_{2\cdot88}$, where the material enclosed in the square brackets represents the contents of the brucite-like layers, and that outside them the interlayer material. The percentage composition corresponding to this formula agrees well with the observed analysis reported by Jambor:

	MgO	MnO	FeO	Fe_2O_3	CO_2	H_2O (molec.)	H_2O (hydrox.)	Total
Calc.	43·0	1·6	0·8	20·8	1·6	5·9	26·2	99·9
Obs.	42·9	1·0	0·7	20·9	1·6	32·0		99·1

The value of 32·0 % for the observed total water content was obtained by subtracting the CO_2 content from the total ignition loss and correcting for the oxidation of the FeO and MnO. Jambor (1969) noted that the TGA curve shows an initial loss of 6·0 % at 260 °C; this corresponds to the loss of the molecular water. He also noted that the CO_2 content was lower than for the Coalinga mineral, and concluded that the CO_3^{2-} present in the latter was partly replaced by OH^-. This conclusion is accepted in the present interpretation; Rouxhet and Taylor (1969) showed that a similar replacement of interlayer CO_3^{2-} by OH^- appears to occur in the type igelströmite, a variety of pyroaurite discovered by Heddle (1879). The total number of interlayer oxygen atoms per six sites is 5·5, against 5·0 for the Coalinga mineral; the increased occupancy is possibly a consequence of the lower CO_3^{2-} content, since the vacancies are probably due to some difficulty in packing the CO_3^{2-} ions and H_2O molecules together without leaving gaps.

Coalingite-K is probably a further member of the brucite–sjögrenite–coalingite series, in which three brucite-like layers occur between each carbonate and water layer (fig. 1, C). This would give an elementary unit about 17·2 Å thick, and the prominent X-ray powder spacings of 5·72 and 4·38 Å observed by Mumpton, Jaffe, and Thompson (1965) could be explained as the third and fourth order basal diffractions respectively. As with coalingite, there are indications of partly random interstratification. The number of elementary units in the cell in the *c*-direction remains to be established. If this hypothesis for coalingite-K is accepted, the idealized formula of this mineral becomes $[Mg_{16}Fe_2(OH)_{36}](CO_3).2H_2O$, and the X-ray density (assuming $a = 3{\cdot}13$ Å) is 2·29 $g.cm^{-3}$. This value agrees satisfactorily with Mumpton, Jaffe, and Thompson's (1965) observed value of about 2·25 $g.cm^{-3}$, and the relatively low Fe:Mg ratio also agrees with their views on the probable composition of this phase. It is proposed to make an investigation to test these predictions.

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