Thermal Decomposition of Sjögrenite and Pyroaurite

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Dedicated to Professor Walter Feitknecht

Summary

When sjögrenite or pyroaurite [$Mg_6Fe_2(OH)_{16}(CO_3) \cdot 4H_2O$ approx.] is heated, the molecular water is lost, reversibly, below 200°C. At 200 to 250°C on static, or 200 to 350°C on dynamic heating little further H_2O or CO_2 is lost, but there are changes in infrared spectrum and DTA effects are observed; X-ray evidence indicates gradual deterioration in crystallinity and gradual decrease of the layer thickness towards a value of about 5 Å. At 250 to 400°C (static) or 300 to 450°C (dynamic) these changes are completed, most of the remaining water and the CO_2 are lost, and MgO and $MgFe_2O_4$ begin to form. The crystallinity of these products gradually increases with rise in temperature up to about 750°C. Both are formed topotactically, that is, in definite crystallographic orientations relative to the starting material.

Introduction

W. Feitknecht's many contributions to the chemistry of basic salts and double hydroxides have included studies on synthetic phases structurally related to the natural minerals sjögrenite and pyroaurite. These minerals are two stacking modifications of typical composition $Mg_6Fe_2(OH)_{16}(CO_3) \cdot 4H_2O$; their crystal structures have recently been determined.[1–3] They are based on brucite-like layers, in which the octahedral sites are filled by both Mg^{2+} and Fe^{3+} ions, and which are separated by intermediate layers composed of the H_2O molecules and CO_3^{2-} ions. Sjögrenite is the 2H-, and pyroaurite the 3R-polytype. In some crystals, the Mg^{2+} and Fe^{3+} are disordered, but in others varying degrees of segregation into regions of differing composition and cation-ordering are observed.[4]

[1] R. Allmann and H.-H. Lohse, *Neues Jb. Min. Mh. 6* (1966) 161.
[2] L. Ingram and H. F. W. Taylor, *Mineral. Mag. 36* (1967) 465.
[3] R. Allmann, *Acta Crystallogr. B24* (1968) 972.
[4] H. F. W. Taylor, *Mineral. Mag. 37* (1969) 338.

No detailed study of the thermal decomposition reactions of these phases appears to have been reported, though some information is available on the behaviour of the corresponding Mg^{2+}–Al^{3+} mineral, hydrotalcite[5,6] and of an apparently related Mg^{2+}–Fe^{3+} mineral, coalingite.[5] The object of the present work was to study the thermal decomposition behaviour of sjögrenite and pyroaurite. In the course of the work, some new facts were established regarding a further Mg^{2+}–Fe^{3+} mineral known as igelströmite.

Material

Two specimens were used. One (A) was from the U.S. National Museum and was labelled "pyroaurite, Långban, Sweden; USNM 93013". It consisted of flakes varying in colour from greyish-white to golden-brown, with a pearly lustre on the cleavage. X-ray single crystal examination showed it to be an intergrowth of pyroaurite and sjögrenite; single crystals or aggregates of both stacking modifications could be found in it. Many gave either superlattice reflections, or splitting of reflections in the c^*-direction attributable to the existence of regions of differing Mg : Fe ratios.[4] An approximate analysis gave Fe_2O_3 27.6, MgO 35.4, CO_2 9.0, H_2O 29.0, total 101.0%; the H_2O and CO_2 results were based on the evolution curves described later. These results are in moderate agreement with the formula

$$Mg_{5.74}Fe_{2.26}(OH)_{16}(CO_3)_{1.13}(H_2O)_{3.6},$$

which demands Fe_2O_3 26.9, MgO 34.5, CO_2 7.4, H_2O 31.1%. Possible reasons for the discrepancies in water and CO_2 contents are discussed later.

The second specimen (B) was from the Geological Survey, London, and was labelled "igelströmite, Haaf Grunay, Shetland; Lindsay 17329". It consisted mainly of dull white flakes with some closely admixed darker material. X-ray examination showed the latter to be serpentine; the white flakes yielded only powder patterns with some preferred orientation, which were identical with those of pyroaurite. No superlattice effects or splitting of reflections was observed, and the layer thickness was 7.83 Å. The status of igelströmite as a distinct mineral species is discussed later; the above X-ray results and other evidence presented later show that the present specimen was pyroaurite.

Water and CO_2 evolution, TGA and DTA

The amounts of water and CO_2 evolved at various temperatures were determined by a gas-volumetric method. The sample (1.0 to 2.5 mg) was placed in a tube connected to a conventional volumetric apparatus fitted with a trap and an oil manometer. The sample was outgassed at room temperature at a pressure of 10^{-3} torr. It was then heated at 50 to 100 °C, the gas evolved on heating being collected in a trap cooled at liquid air temperature. After 20 minutes, the sample tube was isolated from the volumetric apparatus, and the temperature of the trap was raised to dry ice temperature and later on to room temperature so that first the pressure of CO_2 and later the total pressure could be measured. The process was repeated at successively higher furnace temperatures. To avoid errors arising from condensation of water vapour or deviation from ideal gas behaviour, the total pressure was never allowed to exceed 8 torr. The volumetric determination of water was calibrated by the use of various amounts of muscovite mica; the data could then be corrected for adsorption of water by the glass vessel. The corrections amounted to about 10% of the amount of water vapour evolved.

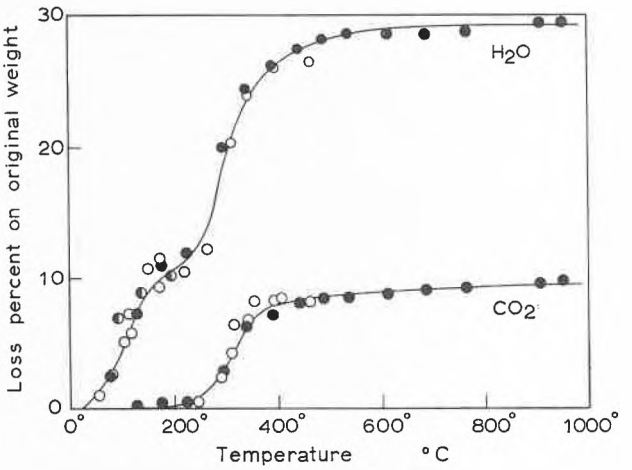

Fig. 1. Water and CO_2 evolution curve for sjögrenite or pyroaurite; specimen A (○), specimen B (●), and specimen A after heating at 175 °C and rehydration at room temperature (◐)

Fig. 1 gives the results for specimens A and B respectively. With specimen B selected white crystals were used. With specimen A a sample was also examined that had been pretreated by heating at 175 °C for 20 minutes and then standing overnight in air at 25 °C. Comparison with the results for the untreated sample shows that the water lost at 175 °C is reabsorbed on standing in air at 25 °C.

Thermogravimetric analysis (TGA) curves were obtained in air using a Dupont 950 apparatus. Fig. 2

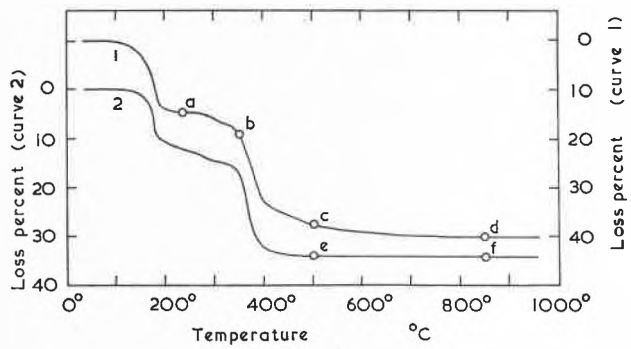

Fig. 2. TGA curve for sjögrenite or pyroaurite; specimen A (curve 2), and specimen B (curve 1). For significance of points *a* to *f*, see text

[5] F.A. Mumpton, H.W. Jaffe and C.S. Thompson *Amer. Mineral. 50* (1965) 1893.
[6] G.J. Ross and H. Kodama, *Amer. Mineral. 52* (1967) 1036.

gives the results. Curve 1 was obtained for a 12.2 mg sample of specimen B, which consisted of selected white crystals. The heating rate was 5 deg C min^{-1}. Curve 2 is for a 2.1 mg sample of specimen A, and was obtained at a heating rate of 3 deg C min^{-1}. It agrees in general form with curve 1, but, because of the smallness of the sample, cannot be considered of high accuracy as regards the weight changes observed.

Water and CO_2 evolution and TGA curves were also obtained for samples of specimen B containing darker material. They showed the same steps as those for white samples, but the heights were lower, and additional steps appeared above 500 °C in the water evolution and TGA curves. These effects are attributable to the presence of serpentine.

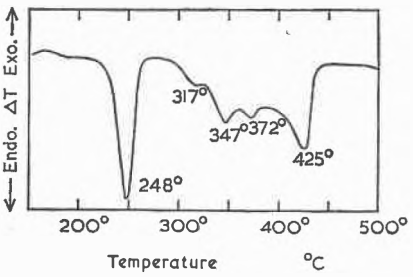

Fig. 3. DTA curve for pyroaurite (specimen B; 15 deg C min^{-1})

Fig. 3 shows a differential thermal analysis (DTA) curve for specimen B, which was obtained in air at a heating rate of 15 deg C min^{-1} using a Dupont 900 apparatus. Selected white crystals were used. The curve is similar in general form to those reported for coalingite and hydrotalcite.[5]

Samples of specimen B were also heated in air for 20 minute periods at various temperatures and examined visually. The colour changes to a pale brown by 200 °C, a somewhat deeper brown or ochre by 500 °C, and a more reddish brown by 1000 °C.

X-ray examination

Crystals of specimen A of approximate size 0.5 mm in their longer dimensions were mounted on silica fibres with a high-temperature adhesive. These were fixed on the goniometer head in such a way that they could be removed and replaced in approximately the same orientation. X-ray photographs were taken to set the crystal about a suitable axis and to establish its orientation; the fibre, with the crystal, was then removed, transferred to an oven for a 30 minute heating period, replaced on the goniometer head, and re-examined. It was thus possible to establish the phases present and their crystallographic orientations relative to that of the starting material.

Some of the crystals examined were sjögrenite and others pyroaurite; some showed splitting of reflections in the c^*-direction and others did not. Heating at temperatures up to 150 °C produced no changes in pattern. At 150 to 200 °C the basal reflections tended to become weaker and more diffuse. No changes in stacking type (i.e. from sjögrenite to pyroaurite or vice versa) were observed. There were also no changes as regards the splitting of reflections in the c^*-direction.

Heating at around 220 °C produced a marked change in the pattern. The hexagonal a-axis of about 3.07 Å remained, but, except for the $000l$ row, the reciprocal lattice was replaced by a pattern of continuous streaks parallel to c^* which became rapidly more diffuse and less intense with increasing distance from the $hki0$ plane. On the $000l$ row, only the first-order reflection was observed; it tended to have a lower spacing than for the unheated mineral (7.3 and 7.7 Å for two crystals heated at 218 °C). Crystals of sjögrenite and pyroaurite yielded products giving identical patterns when heated under the same conditions at or above this temperature.

Heating at 220 to 400 °C caused the pattern of the hexagonal phase to become progressively more indistinct and the layer thickness to became progressively smaller. Fig. 4 gives the values of the basal spacing obtained for a crystal of sjögrenite heated for 30 minute periods at successively higher temperatures. By 400 °C the pattern of the hexagonal phase had almost disappeared and the basal reflection was no longer visible.

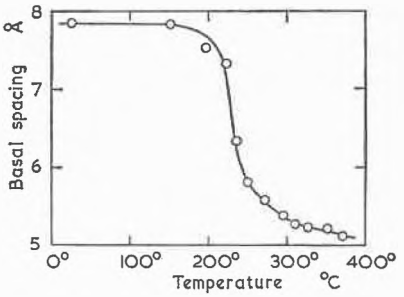

Fig. 4. X-ray basal spacings of the hexagonal phase after heating in air for 20 minute periods at various temperatures

At temperatures above about 350 °C, the reflections of MgO and $MgFe_2O_4$ begin to appear. Below about 400 °C they are weak and diffuse, the only ones visible being the 311, 400 and 440 reflections of the $MgFe_2O_4$. The second and third of these coincide respectively with the 200 and 220 reflections of MgO; the patterns were too diffuse for any separation of corresponding MgO and $MgFe_2O_4$ reflections to be detectable. With increasing temperature, the reflections become sharper, stronger, and more numerous, and by about 750 °C sharp and complete patterns of both are obtained. A Guinier photograph of a sample of specimen B heated to 1000 °C showed that the MgO and $MgFe_2O_4$ were present as separate phases. The single crystal photographs showed that, over the whole temperature range in which they are present, both phases are formed topotactically, that is, in definite crystallographic orientations relative to the starting material. There were two orientations for

both phases, identical with those observed in the formation of MgO from $Mg(OH)_2$.[7,8]

A few observations were also made on samples that had been heated dynamically to various temperatures. Heating was carried out on the thermobalance to selected points on the weight-loss curve, which was recorded normally; the samples were then removed for examination. It was possible to lower the temperature from the final point reached on the curve to room temperature within one minute. Using specimen B, a sample heated to 235 °C (Fig. 2, point *a*) gave a pattern identical with that of the starting material. One heated to 350 °C (point *b*) gave a very weak and diffuse pattern showing only a few *hk*-band reflections and a basal reflection of spacing 5.5 Å. One heated to 500 °C (point *c*) gave a weak pattern showing the two strongest reflections of MgO or Mg_2FeO_4, and one heated to 850 °C (point *d*) gave the reflections of MgO and $MgFe_2O_4$. The results at 500° and 850 °C were confirmed with specimen A (points *e* and *f*).

Infrared examination

For this part of the work, a portion of specimen A was used which was shown by an X-ray rotation photograph to be sjögrenite. Absorption spectra were obtained using a Beckmann IR-12 instrument with a beam condenser, using the KBr disk method (0.5 mg of the powdered sample with 50 mg of KBr in an 8 mm diameter disk). Fig. 5 gives the results for the mineral before heating (curve *S* 25 °C) and after heating for 30 minute periods in air at successively higher temperatures. The same sample was used throughout, the disk being crushed before each heating period and re-pressed immediately afterwards. For comparison, spectra were also obtained for MgO, $Mg(OH)_2$ and $MgFe_2O_4$ (curves *P*, *B* and *F* respectively).

The spectrum for unheated sjögrenite (curve *S* 25 °C) agrees substantially with that given by MUMPTON *et al.*[5] The hydroxyl stretching band, which is broad, peaks at a frequency (3450 cm^{-1}) distinctly lower than that of brucite (3700 cm^{-1}; curve *B*), confirming that the hydroxyl groups are hydrogen-bonded in sjögrenite.[2] The stretching and bending bands of the molecular water occur at 3100–3200 and 1650 cm^{-1} respectively; the band at about 700 cm^{-1} is attributed to a librational mode of the water molecule.[9] The assignments of these four bands were confirmed by studying the effects of H/D isotope exchange.

The results show that loss of molecular water is complete by about 200 °C, and that dehydroxylation occurs above this temperature. Some hydroxyl appears to remain at 600 °C. This could possibly be due to rehydroxylation but is consistent with the water evolution curve (Fig. 1). The frequency of the hydroxyl stretching band remains unchanged over the entire temperature range in which it is observed.

The bands at 1300–1600 cm^{-1} are attributed to the CO_3^{2-} ion. The fact that the unheated mineral shows only a single peak in this region suggests that the site symmetry of the CO_3^{2-} ion is $\bar{6}2m$ or 32 and not 3 or $2mm$.[10,11] This agrees with the structure proposed by INGRAM and TAYLOR,[2] which indicates site symmetry $\bar{6}2m$ for the CO_3^{2-} ion. Heating at 137 °C does not affect the CO_3^{2-} band, but at 185 to 308 °C progressive changes occur which indicate that the environment of the ion becomes less symmetrical. The CO_3^{2-} ion disappears, simultaneously with most of the hydroxyl, between 250 and 400 °C.

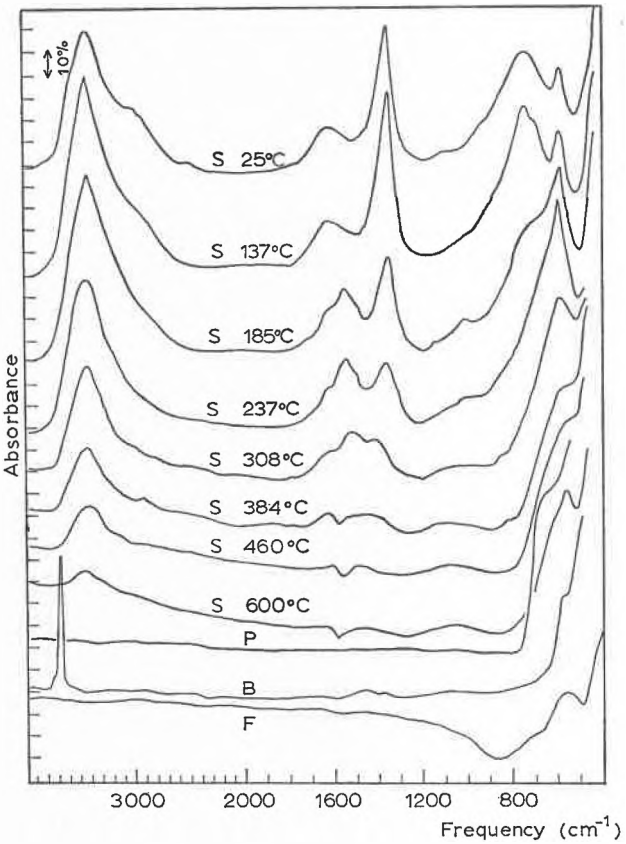

Fig. 5. Infra-red absorption spectra. Curves *S*: sjögrenite, unheated and after heating in the KBr disk for 30 minute periods at the stated temperatures. Curves *P*, *B* and *F*: MgO, $Mg(OH)_2$ and $MgFe_2O_4$, respectively

In accordance with FARMER's[12] conclusion for brucite, the bands at 400–600 cm^{-1} are attributed to Mg–O vibrations. The bands of the 600 °C product in this region are similar to those of MgO and $MgFe_2O_4$ (curves *P* and *F*).

[7] J. GARRIDO, *Ion. Rev. Espan. Quim. Aplic. 11* (1951) 206, 220, 453.
[8] M. C. BALL and H. F. W. TAYLOR, *Mineral. Mag. 32* (1961) 754.
[9] P. A. GIGUÈRE and K. B. HARVEY, *Can. J. Chem. 34* (1955) 798.
[10] K. NAKAMOTO, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, London 1963, p. 328.
[11] H. H. ADLER and P. F. KERR, *Amer. Mineral. 48* (1963) 839.
[12] V. C. FARMER, *Mineral. Mag. 31* (1958) 829.

Discussion

It will be convenient to discuss the thermal reactions of pyroaurite of sjögrenite in terms of three stages, viz: (i) loss of molecular water, (ii) structural alteration and loss of hydroxyl water and CO_2, and (iii) crystallization of oxide products. These are now considered in turn.

Stage I: Loss of Molecular Water

The water evolution curves (Fig. 1) show an initial step at 50 to 200 °C, and the TGA curves (Fig. 2) show a corresponding one at 100 to 200 °C. The infrared results (Fig. 5) show that these steps are wholly, or very largely, due to loss of molecular water. The process is represented on the DTA curve (Fig. 3) by the initial large endotherm at 248 °C. The differences in the temperature ranges over which the effects occur are attributable to differences in heating rate and partial pressure of water vapour among the three methods.

The TGA curve for specimen B indicates a loss of 13.9% below 200 °C; the water evolution curve shows a lower value but this can probably be attributed to partial dehydration during the preliminary outgassing. The TGA value is above the theoretical amount (9.6%) corresponding to the formula

$$Mg_{5.74}Fe_{2.26}(OH)_{16}(CO_3)_{1.13}(H_2O)_{3.6}$$

Possibly some dehydroxylation occurs below 200 °C; the fact that the material begins to turn brown by this temperature lends support to this view.

The water evolution experiments show that the loss of molecular water is, at least in part, reversible. The X-ray patterns obtained for samples cooled from 200 °C or below must relate to rehydrated material; either no changes in unit cell parameters accompany the loss of molecular water, or if they do they are reversible. High-temperature X-ray photographs would be needed to settle this point. The present evidence shows that loss of the molecular water does not result in changes or disorder in the layer stacking.

Stage II: Structural Alteration and Loss of Hydroxyl Water and CO_2

The first definite indications of alteration in the sjögrenite or pyroaurite structure, other than the loss of molecular water, are provided by the infrared spectra (Fig. 5), which show that changes in the environment of the carbonate ions begin to occur by 185 °C for sjögrenite. These changes, which become progressively more marked up to 308 °C, are possibly caused by the disappearance of the water molecules. The X-ray evidence shows that more profound alteration occurs above 220 °C; the results can probably be interpreted as showing the formation of a randomly interstratified structure, in which some layers retain the three sheets of oxygen or hydroxyl initially present, while others contain only two. The general weakness of the X-ray patterns suggests that much amorphous material is also present. With increase in temperature, the ratio of amorphous to crystalline material increases, as does that of two- to three-sheet layers in the interstratified structure; these changes are well-advanced by 300 °C for static, or 350 °C for dynamic heating conditions. They can probably be associated with the endotherms at 317, 347 and 372 °C on the DTA curve (Fig. 3). By 400 °C for static heating conditions, the last traces of the original structure have disappeared.

The water evolution curve (Fig. 1) shows a second step at 200 to 500 °C, and most of the CO_2 is lost in the same range of temperature. A little H_2O and CO_2 are retained up to 1000 °C. The corresponding step on the TGA curve (Fig. 2) is at 350 to 450 °C, and the corresponding endotherm on the DTA curve (Fig. 3) at 425 °C. The infrared evidence (Fig. 5) confirms that these effects are associated with the loss of the hydroxyl and carbonate ions. The observed amounts of water and CO_2 lost above 200 °C are in poor agreement with the calculated values; for specimen B, the curves in Fig. 1 indicate H_2O 18.5%, CO_2 9.0% (calculated for $Mg_{5.74}Fe_{2.26}(OH)_{16}(CO_3)_{1.13}(H_2O)_{3.6}$, H_2O 21.5%, CO_2 7.4%). Because of the shortage of material, the reasons for these discrepancies were not established. Possible causes include experimental errors, inhomogeneity of material especially in regard to Mg : Fe ratio, and the loss of some of the hydroxyl water below 200 °C which has already been mentioned.

More detailed interpretation of these results is difficult. At first sight, the evidence appears to show that the structural changes indicated by the X-ray results take place before the main evolution of hydroxyl water and CO_2. If this is so, the two-sheet layers in the interstratified structure do not consist of the product of dehydroxylation and decarbonatation, but must result from some internal rearrangement. In this connection it may be noted that MUMPTON *et al.*[5] postulated such a rearrangement for the somewhat analogous case of coalingite. However, caution is needed in comparing temperatures recorded in the different experimental methods used; even where the period of heating at a given temperature is the same, reaction may proceed to different extents because of differences in crystal size, ease with which evolved gases can escape, or other factors. It is therefore also possible that the interstratified structure is formed as the product of the dehydroxylation and decarbonatation process.

Whichever of these views is correct, the fact that an interstratified structure is formed shows that reaction does not begin exclusively at the surface of the crystal, but at sites which are from 1 to 100 layers apart from each other in the *c*-direction. The interstratification shows also that the nuclei grow more rapidly in the *ab*-plane than in the *c*-direction.

Stage III: Crystallization of Oxide Products

The X-ray evidence shows that MgO and $MgFe_2O_4$ begin to form, topotactically, by about 350 °C; in both cases, crystallinity is low at this temperature and improves gradually in the range up to about 750 °C. The results throw little light on the detailed mechanism of formation of these phases, but it is clear that this cannot be the inhomogeneous one suggested by BALL and TAYLOR[8] for the dehydroxylation of brucite. The process is probably one of nucleation and growth, the orientation of the product crystals being controlled initially by nucleation on surfaces of the interstratified product. It is unlikely that the structure of the latter is based on any well-ordered and approximately close-packed oxygen framework, and virtually certain that the amorphous phase, which seems to make up a large proportion of the material, is not. This also applies to the dehydrated phase obtained around 200 °C. The topotactic character of the reaction cannot, therefore, be due to the substantial preservation of any such framework. This point is of some importance, because it has sometimes been suggested that reactions of this type proceed topotactically only if there is an oxygen framework which is substantially preserved and within which cations can migrate, and that the existence of topotaxy in such cases therefore necessarily implies an inhomogeneous mechanism.

[13] HEDDLE, *Mineral. Mag.* 2 (1879) 106.

A note on igelströmite

HEDDLE,[13] who discovered igelströmite, considered it to be a mineral species distinct from pyroaurite on the ground that it contained little or no CO_2; he reported a composition approximating to $Mg_3Fe(OH)_9 \cdot 3H_2O$ (the mean of three analyses gave H_2O 39.6%, CO_2 0.7%). The present results agree substantially with this as regards the total of water and CO_2, but indicate the presence of 9.8% CO_2. Together with the X-ray evidence, this indicates that the specimen examined was pyroaurite. The locality (Haaf Grunay) is the type locality for igelströmite, and the result provides no support for the view that the latter is a distinct mineral species. At the same time, there is no positive reason for doubting HEDDLE's analyses. The composition of the material possibly varies sharply from point to point, and the specimens that he examined could have contained OH^- in place of CO_3^{2-} as the principal interlayer anion. Comparison of optical data would probably have clarified this question, but unfortunately HEDDLE did not report these. The mineral namely igelströmite should be reserved for the essentially carbonate-free material, should its existence later be confirmed.

Acknowledgments

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