

A reinvestigation of takovite, a nickel aluminum hydroxy-carbonate of the pyroaurite group

DAVID L. BISH AND G. W. BRINDLEY

Department of Geosciences and Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania 16802

Abstract

Samples from Takovo, Serbia (the type locality); Perseverance Mine, Agnew, Australia; and Var, France, were examined by X-ray powder diffraction, infrared and optical absorption spectroscopy, and thermogravimetric and chemical analysis. X-ray powder data are indexed with a hexagonal unit cell, and for the Takovo sample, $a = 3.0250$, $c = 22.595$ Å; the observed spacings conform with rhombohedral symmetry. The observed cell parameters are closely similar to those of pyroaurite and hydrotalcite. Spectroscopic and chemical data confirm the presence of both molecular water and carbonate ions. The compositions of the Australian and Var samples approximate to $\text{Ni}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3, \text{OH}) \cdot 4\text{H}_2\text{O}$. Similar synthetic materials have been prepared by adding nickel and aluminum chlorides to a CO_2 -saturated solution of NaOH and heating the product for 10 days or one month at 200–250°C and 1500 bars water-vapor pressure.

Introduction

Takovite was named by Maksimovic (1957) and was described as a nickel hydroaluminate with composition $\text{Ni}_5\text{Al}_4\text{O}_2(\text{OH})_{18} \cdot 6\text{H}_2\text{O}$. The properties and genesis of the mineral were discussed in subsequent papers (Maksimovic 1968, 1970, 1973). The formula was obtained after subtracting SiO_2 as quartz, 2 percent goethite, and 0.8 percent calcite. An X-ray pattern of 17 lines was given, and five reflections from a basal spacing of 7.6 Å were recorded.

The similarity of the X-ray pattern of takovite to those of synthetic Mg,Al hydroxy-carbonates (Brown and Gastuche, 1967) and of minerals of the pyroaurite and sjögrenite groups (Mumpton *et al.*, 1965; JCPDS Card #14-293) led us to consider that the formula given by Maksimovic might be rewritten $\text{Ni}_5\text{Al}_4(\text{OH})_{22} \cdot 4\text{H}_2\text{O}$, and furthermore that if $(\text{CO}_3)^{2-}$ replaced $2(\text{OH})^-$, then the resulting formula, $\text{Ni}_5\text{Al}_4(\text{OH})_{20}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, approached that of a nickel hydrotalcite, $\text{Ni}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$. The differences, however, are such that a further investigation of takovite seemed necessary, and in particular the question whether takovite contained carbonate ions had to be resolved.

The extensive literature on the pyroaurite and sjögrenite groups of minerals has been surveyed by Allmann (1970) and Taylor (1973). A nickel-contain-

ing mineral, reevesite, with composition $\text{Ni}_6\text{Fe}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ has been discussed by White *et al.* (1967) and by De Waal and Viljoen (1971), and a Ni,Zn mineral eardleyite, $(\text{Ni,Zn})_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ by Anderson and Whelan (1962), but a specific Ni,Al mineral seems not to have been described. Takovite may in fact be this mineral, and the present results lead to this conclusion.

Materials studied

Natural materials

Four samples of natural takovite have been studied. One sample, made available by Dr. E. H. Nickel, CSIRO., Wembley, W. Australia, was from the Perseverance Mine, Agnew, Australia. This sample contained poorly crystalline kaolinite as an impurity. A very small sample from Var, France (Var I), given by Dr. Z. Maksimovic, consisted of blue-green particles with associated boehmite. A second and larger sample from Var (Var II) was obtained through the assistance of Mr. G. H. Sabiston, Mandeville, Jamaica, Mr. H. Roy Hose, Boissano, Italy, and Mr. Louis Gallay, Aix-en-Provence, France; this sample was a thin green coating on bauxite and was associated with boehmite and kaolinite. A few mg of takovite from the type locality, Takovo, were sup-

plied by Dr. Maksimovic. This sample, which became available only when the investigation was nearly complete, was of great value in proving the identity of the Australian and Var samples with the named material, for which the presence of carbonate ions had not been established.

Synthetic materials

A synthetic Ni-Al hydroxy-carbonate was prepared in order to compare its properties with those of takovite. A solution of 0.75M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.25M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was dripped into a 1.0M NaOH, CO_2 -saturated, solution. The resultant precipitate, after washing, was heated in hydrothermal bombs at 200°C and 1500 bars H_2O pressure for ten days and at 250°C and the same H_2O pressure for one month. Comparison of the synthetic and the natural materials revealed their close similarity.

Nitrate and sulfate analogues also were prepared, but, except for the differing basal spacings and the lack of CO_2 , these had properties essentially similar to those of the Ni-Al hydroxy carbonate.

Results

X-ray powder data, unit-cell parameters, and density

Diffraction patterns of the Australian and Var samples were recorded with Ni-filtered $\text{CuK}\alpha$ radiation at $1^\circ(2\theta)/\text{min}$, and Debye-Scherrer powder photographs were recorded of the Australian and Takovo samples. The main characteristics of all the patterns were very similar and agreed with the original data of Maksimovic (1957) for the reflections which he recorded. The data also indicated the presence of poorly crystallized kaolinite in the Australian and Takovo samples and appreciable boehmite and a lesser amount of kaolinite in the Var samples.

Table I records the X-ray data for samples from Takovo, Australia, and Var, and the original data of Maksimovic (1957). Also given are data for the synthetic Ni,Al hydroxy carbonate, and for hydrotalcite, $\text{Mg}_6\text{Al}_2(\text{OH})_{16} \cdot \text{CO}_3 \cdot 4\text{H}_2\text{O}$ (Mumpton *et al.*, 1965), and pyroaurite, $\text{Mg}_6\text{Fe}_2(\text{OH})_{16} \cdot \text{CO}_3 \cdot 4\text{H}_2\text{O}$ (JCPDS Card #14-293). The takovite patterns are similar to those of hydrotalcite and pyroaurite and have been indexed on a similar hexagonal cell. Unit-

Table I X-ray diffraction data for takovite and related materials

Takovite ^{1,4}		Takovite ⁴		Takovite ⁴		Takovite ⁵		Ni-Al hydroxy-carbonate ⁵		Hydrotalcite ^{2,4}		Pyroaurite ^{3,4}	
Takovo, Yugoslavia		Takovo, Yugoslavia		Agnew, Australia		Var, France		synthetic		Snarum, Norway		Långban, Sweden	
d	I/I ₀	d	I/I ₀	d	I/I ₀	d	I/I ₀	d	I/I ₀	d	I/I ₀	d	I/I ₀
7.566	100	7.54	100	7.50	100	7.50	100	7.72	100	7.83	10	7.77	100
3.767	90	3.77	70	3.76	50	3.75	40	3.87	40	3.92	9	3.89	80
2.603	40	2.606	5	2.60	5	2.595	5	2.63	10	2.62	6	2.62	50
2.552	90	2.553	80	2.551	60	2.544	30	2.57	20	---	---	---	---
2.375	50b*	2.377	15	2.372	5	2.368	10	---	---	---	---	---	---
2.264	80	2.268	70	2.266	50	2.258	30	2.295	20	2.31	6	2.33	50
2.031	20	2.037	10	2.034	5	---	---	2.056	6	---	---	---	---
1.917	90	1.921	60	1.920	35	1.916	25	1.954	10b	1.97	8	1.97	50
---	---	1.888	1	1.879	2	---	---	1.929	7b	---	---	---	---
1.708	70b	1.711	25	1.708	5	1.708	15	1.752	15	1.755	3	1.76	10
1.613	60b	1.617	20	1.616	5	1.614	10	---	---	1.662	3	1.66	10
1.510	80	1.513	50	1.512	10	1.510	15	1.520	15	1.535	4	1.55	20
1.481	80	1.483	50	1.483	10	1.481	20	1.492	15	1.506	5	1.52	20
---	---	1.448	20	1.445	5	1.449	10	---	---	---	---	1.49	10
1.401	30vb	1.404	30	1.403	10	1.401	5b	1.415	10	1.427	2	1.44	10
1.373	60	1.374	15	1.373	5	1.372	5b	---	---	---	---	1.42	10
---	---	1.301	25	1.303	5	1.308	10	---	---	1.322	1	1.33	10
---	---	1.288	3	---	---	---	---	---	---	---	---	---	---
1.256	50	1.259	30	1.258	5	1.255	5	---	---	1.302	1	1.29	10
1.241	10b	1.243	20	1.243	5	1.241	5	---	---	1.282	3	1.28	10
---	---	1.214	5	1.214	5	---	---	---	---	---	---	---	---
1.183	40b	1.190	15	1.188	5	---	---	---	---	1.212	2	1.22	10
		Plus 20 lines to 0.7982		Plus 18 lines to 0.8108									

* b = broad vb = very broad

1 Data from Maksimovic (1957)

2 Data from Mumpton *et al.* (1965)

3 Data from J.C.P.D.S. Card #14-293

4 Powder camera data

5 Diffractometer data

Table 2 Observed and calculated powder data and unit-cell parameters for takovite from Takovo, Serbia

hkl	I/I ₀	d _{obs}	d _{calc}	hkl	I/I ₀	d _{obs}	d _{calc}
003	100	7.54	7.53	208	15	1.190	1.189
006	70	3.77	3.77	02.10	5	1.133	1.133
101	5	2.606	2.603	20.11	10	1.105	1.105
012	80	2.553	2.553	10.19	2	1.083	1.083
104	15	2.377	2.377	11.15	1	1.064	1.067
015	70	2.268	2.267	02.13	5	1.045	1.046
107	10	2.037	2.034	20.14	2	1.017	1.017
018	60	1.921	1.921	122	10	0.9863	0.9866
00.12	1	1.888	1.882	125	15	0.9665	0.9675
10.10	25	1.711	1.711	217	2	0.9460	0.9469
01.11	20	1.617	1.617	128	10	0.9335	0.9346
110	50	1.513	1.513	21.10	5	0.9061	0.9071
113	50	1.483	1.483	12.11	5	0.8912	0.8921
10.13	20	1.448	1.448	300	3br**	0.8733	0.8735
116	30	1.404	1.404	303	5	0.8670	0.8677
01.14	15	1.374	1.374	21.13	3br	0.8597	0.8605
202	25	1.301	1.302	306	2	0.8506	0.8509
119	3	1.288	1.295	12.14	1	0.8450	0.8442
205	30	1.259	1.258	01.26	2br	0.8244	0.8249
10.16	20	1.243	1.243	21.16	2br	0.8092	0.8109
027	5	1.214	1.214	11.24	2br	0.7982	0.7993

$$a_0 = 3.0250 (1) \text{ \AA} \quad c_0 = 22.595 (3) \text{ \AA} \quad \text{Volume} = 179.06 (2) \text{ \AA}^3$$

* Powder camera, 114.6 mm dia., CuK α radiation, spacings in \AA , I/I₀ visual estimate, hkl hexagonal indices

** br = broad line

cell parameters were refined by the least-squares refinement program of Appleman and Evans (1973). The observed and calculated spacings and the cell parameters for the Takovo sample are given in Table 2. The indices are consistent with rhombohedral symmetry. Refined cell parameters for the Australian material are; $a = 3.0280(4)$ $c = 22.45(2)$ \AA , volume = $178.31(15) \text{ \AA}^3$.

The density of the Australian sample determined by pycnometer measurements is $\sim 2.70 \text{ g cm}^{-3}$. The value calculated from the unit-cell parameters, chemical composition, and $Z = 3/8$ is 2.79. The lower experimental value can probably be attributed to the small sample available, the aggregate nature of the material, and the kaolinite impurity.

Infrared data

Infrared spectra of all four samples were obtained using a Perkin-Elmer 621 spectrometer and a KBr pellet technique. Spectra of the Takovo, Australian, and Var II samples are shown in Figure 1. Absorptions arising from kaolinite and boehmite impurities are indicated in the figure. The patterns agree with that of hydroxalcite given by Mumpton *et al.* (1965) and of sjögrenite given by Rouxhet and Taylor (1969).

The main features of the takovite patterns are as follows: A sharp OH stretching frequency occurs at about 3400 cm^{-1} . A broad band centered around 3000 cm^{-1} suggests the presence of hydrogen-bonded water molecules (see discussion by White, 1971) with an OH-O distance of about 2.69 \AA based on the Lippincott-Schroeder curve. A similar band occurs in the hydroxalcite spectrum and may correspond to the H₂O-CO₃ bond distance, given as 2.71 \AA by Allmann and Jepson (1969). An H₂O bending vibration occurs at 1600 cm^{-1} . Of special interest is the 1350 cm^{-1} frequency which corresponds to the ν_3 frequency of the CO₃²⁻ ion. This band is double for all four takovites examined with vibrations at 1350 and 1390 cm^{-1} . This splitting suggests that the site symmetry of the CO₃²⁻ ion is lower in takovite than in sjögrenite. Strong absorption around 800 cm^{-1} was attributed by Rouxhet and Taylor to a librational mode of the water molecule but could also be the ν_2 absorption of the CO₃²⁻ ion; this absorption is absent in the spectrum of HCl-treated material. Vibrations at lower frequencies can be attributed to cation-oxygen vibrations. An unexplained absorption occurs between 1250 cm^{-1} and 1270 cm^{-1} in the Australian and Takovo spectra.

Spectra of the synthetic materials are similar to those of the natural materials after subtracting absorptions due to impurities, but their unsplit CO₃²⁻ ν_3 vibration more closely resembles that of sjögrenite. The spectrum of HCl-treated takovite is of interest in that it is similar to that of the untreated material except for the absence of the CO₃²⁻ vibrations. The mineral is slowly attacked by cold dilute HCl, and when small fragments are observed under the microscope the very slow evolution of gas bubbles, presumably CO₂, can be seen. Evidently the main structure of takovite is not destroyed by HCl; a slightly modi-

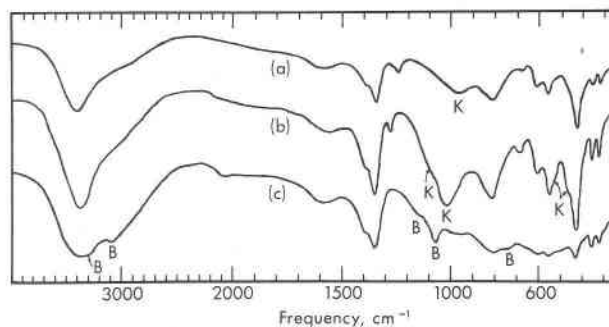


Fig. 1 Infrared absorption spectra for takovite samples from (a) Takovo, (b) Australia, and (c) Var. Absorptions due to kaolinite and boehmite are indicated by K and B respectively.

fied X-ray diffraction pattern with a basal spacing of 7.70Å is obtained.

Optical absorption spectra

Spectra were obtained using the reflectance attachment of a Beckman DK-2A spectrophotometer. Analysis of the spectra by crystal-field theory gives a value $\sim 896\text{ cm}^{-1}$ for Dq , which is consistent with Ni^{2+} in a normal oxide or hydroxide structure. (Dq is a measure of the interaction between the cation and its surroundings and is a function of metal ion-anion distance and coordination number.) From the plot of Dq vs. $M\text{-O}$ bond distance given by Faye (1974), the Ni-OH bond distance in takovite is estimated as $2.03 \pm 0.015\text{Å}$. This value agrees closely with the metal-OH distance in sjögrenite given by Allmann and Lohse (1966) as 2.06Å, particularly when the slightly smaller ionic radius of Ni^{2+} as compared with Mg^{2+} is considered (Shannon-Prewitt radii are Mg^{2+} , 0.86Å, Ni^{2+} , 0.83Å). No evidence is obtained for the presence of appreciable Ni^{3+} ions.

Optical data

The Australian takovite is uniaxial negative with a mean refractive index of 1.594. Several particles gave biaxial figures with $2V$ in the range $0\text{--}10^\circ$. Similar results were reported by Frondel (1941) for pyroaurite and sjögrenite.

Thermal data with combined X-ray and IR analyses

Thermogravimetric analyses of the Australian and Var II materials have been made, using a recording microbalance with controlled rate of temperature increase of $5^\circ\text{C}/\text{min}$. The recordings were made in normal air atmospheres and with samples of about 10 mg weight. Figure 2 shows percentage weight losses of the samples from 25° to 1000°C . The curves are similar, but the reactions of the Var II sample take place at about 50°C higher temperatures than the Australian sample. We have no certain explanation for this difference in reaction temperatures other than a particle- or crystal-size effect.

Above 100°C two principal weight losses are clearly seen from around $150\text{--}250^\circ\text{C}$ and $250\text{--}350^\circ\text{C}$. Less well-defined losses occur around $350\text{--}500^\circ\text{C}$ for the Australian sample and $400\text{--}600^\circ\text{C}$ for the Var II sample. There is also a small continued weight loss from 600° to about 800°C . The interpretation of these weight losses with the help of X-ray and IR data for separately heated samples is complicated by the presence of impurities, kaolinite in the Australian

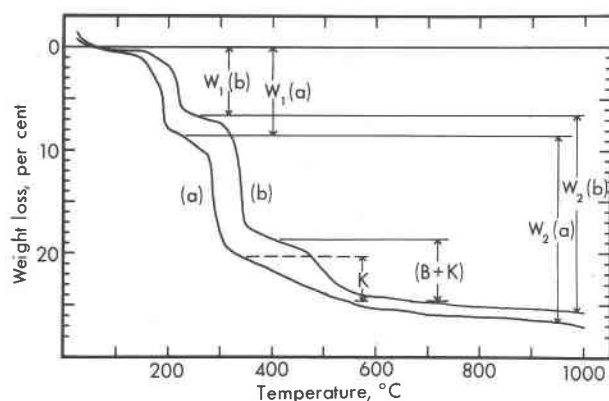


Fig. 2. Thermogravimetric curves for (a) Australian, (b) Var II samples. W_1 = weight loss due to molecular water. W_2 = combined higher temperature weight loss. K = weight loss due to kaolinite impurity. $B + K$ = weight loss due to boehmite + kaolinite impurities.

sample, and boehmite with kaolinite in the Var II sample.

The first weight loss, W_1 , (8.55% for the Australian sample, 6.6% for the Var II sample) corresponds to a loss of molecular water as shown by the IR-spectra (Fig. 3). The absorptions at about 800 cm^{-1} and 1600 cm^{-1} , attributed by Rouxhet and Taylor (1969) to the bending and librational modes respectively of molecular H_2O , have largely gone by 200°C in the Australian sample and 250°C in the Var II sample. In addition, the CO_3^{2-} ν_3 band persists but shows splitting, and the hydroxyl stretching band is unchanged. X-ray data show that the basal spacing is reduced from 7.5Å to about 6.6Å and that the water loss is not completely reversible.

The second prominent step in the weight-loss curves is associated with the loss of CO_2 and hydroxyl water, which is largely complete when the second plateau is reached around $350\text{--}400^\circ\text{C}$. The less well-defined losses in the $350\text{--}600^\circ\text{C}$ range are associated mainly with the water losses from the kaolinite and boehmite impurities.

For the Australian sample, where kaolinite appears to be the only significant impurity, the SiO_2 content (14.04%, see later) corresponds to 30.2 percent kaolinite and 4.21 percent H_2O . A weight loss of this magnitude, marked K in Figure 2, corresponds to the weight loss of the sample from $350\text{--}550^\circ\text{C}$. The total weight loss, $W_2 = 18.7$ percent, from $225\text{--}1000^\circ\text{C}$ is taken as the loss due to CO_2 plus hydroxyl water plus 4.2 percent from the kaolinite impurity. Then $\text{CO}_2 + \text{H}_2\text{O}$ (hydroxyl) = 14.5 percent.

In the case of the Var II sample, we take the weight

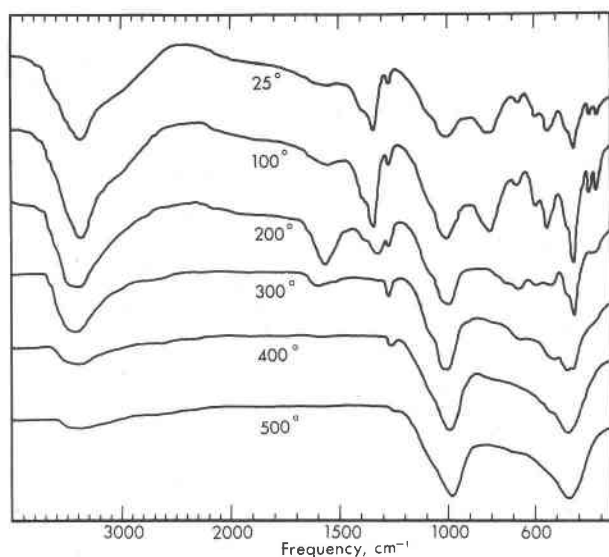


Fig. 3. Infrared absorption spectra of Australian takovite sample after previous heatings at temperatures shown.

loss from 400–650°C, marked *B + K* in Figure 2, as arising from boehmite and kaolinite. The SiO₂ content (3.72%, see later) corresponds to 8.0 percent kaolinite and 1.12 percent H₂O. The total percent of impurity water, *B + K* in Figure 2, is 5.8 percent of which 4.7 percent is attributed to boehmite (corresponding to 31.5% boehmite). Then the total weight loss, *W*₂ = 19.1 percent, from 250–1000°C, is due to CO₂ plus hydroxyl water, plus 5.8 percent water from kaolinite and boehmite. Then CO₂ + H₂O (hydroxyl) = 13.3 percent.

These data form part of the chemical analyses given in the following section where they are discussed further.

Chemical analyses and derivation of structural formulae

Samples of the Australian and Var II takovites were heated to 1100°C, and 40 mg of ignited material was analyzed using the LiBO₂ fusion technique of Suhr and Ingamells (1966) and a Perkin Elmer 403 atomic absorption spectrophotometer. The ignition losses were taken from the thermogravimetric curves. The CO₂ contents were determined by a gas volumetric method in which CO₂ was evolved by dissolution of the minerals in phosphoric acid. The CO₂ contents are considered accurate to ± 5 percent. As explained in the preceding section, the minerals are considered to contain molecular water liberated between about 150 and 250°C, and hydroxyl water together with CO₂ liberated at higher temperatures.

With known values for the CO₂ contents, the hydroxyl water is then known.

Table 3 lists the total chemical analyses and the separate evaluation of the components making up, in each case, the total ignition loss. From these data we proceed to evaluate chemical formulae for the two takovite samples on the assumption of 8 cations/formula unit.

Australian takovite. The cation composition is evaluated as (Ni_{5.54}Mg_{0.19})(Al_{1.93}Fe_{0.35}) which corresponds to a ratio R²⁺/R³⁺ of 5.73/2.28; this ratio approaches the ratio 6/2. The remaining composition O_{9.15}(H₂O)_{7.64}^(a)(CO₂)_{0.80}(H₂O)_{5.66}^(b), where (a) is hydroxyl water and (b) is molecular water, can be reorganized to (OH)₁₆[(CO₃)_{0.80}(OH)_{0.70}](H₂O)_{4.95}^(b). In arriving at this result 0.71 (H₂O)^(b) is transferred to the hydroxyl water (a). This is equivalent to a small amount of hydroxyl water, 0.71 H₂O, being lost along with the molecular water. Evidence for partial dehydroxylation below 200°C was found also by Rouxhet and Taylor (1969) for sjögrenite.

Var II takovite. The cation composition,

Table 3 Chemical analyses of Australian and Var II takovites

	Australian takovite		Var II takovite	
	Total chemical analysis	Revised total ¹	Total chemical analysis	Revised total ²
SiO ₂	14.04	0.00	3.72	0.00
Al ₂ O ₃	20.18	8.26	37.53	7.62
Fe ₂ O ₃	2.33	2.33	0.54	0.54
Cr ₂ O ₃	0.00	0.00	0.08	0.08
MgO	0.63	0.63	0.25	0.25
NiO	34.73	34.73	31.97	31.97
CaO	0.14	0.14	0.21	0.21
Na ₂ O	0.24	0.24	0.00	0.00
K ₂ O	0.07	0.07	0.01	0.01
L.O.I.	27.27	23.06	25.68	19.84
Total	99.63	69.46	99.99	60.52
Analysis of ignition loss			Analysis of ignition loss	
H ₂ O (hydroxyl)		11.55		10.16
H ₂ O (molecular)		8.56		6.61
CO ₂		2.95		3.07
Total		23.06		19.84

¹Total analysis minus 30.2% kaolinite

²Total analysis minus 31.5% boehmite and 8.0% kaolinite

($\text{Ni}_{5.78}\text{Mg}_{0.08}$) ($\text{Al}_{2.02}\text{Fe}_{0.09}\text{Cr}_{0.01}$), corresponds to a ratio R^{2+}/R^{3+} of 5.87/2.12, which approaches even closer to the ratio 6/2 than for the Australian sample. The remaining composition, $\text{O}_{9.05}(\text{H}_2\text{O})_{7.63}^{(a)}(\text{CO}_2)_{0.95}(\text{H}_2\text{O})_{4.96}^{(b)}$ can be reorganized to $(\text{OH})_{16}[(\text{CO}_3)_{0.95}(\text{OH})_{0.20}](\text{H}_2\text{O})_{4.49}^{(b)}$. Again, a small amount of hydroxyl water, $0.47 \text{ H}_2\text{O}$, is assumed to be lost with the molecular water.

Both formulae come close to the composition $\text{Ni}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3) \cdot 4\text{H}_2\text{O}$, especially when the details involved in analyzing the thermogravimetric curves are considered. The formula of the Australian takovite, for which only kaolinite is a significant impurity, is established with greater certainty than that of the Var sample for which two impurities are involved. The estimation of the boehmite from the thermogravimetric curve is the main source of uncertainty and may affect the value calculated as 31.5 percent to the extent of ± 2 –3 percent. Table 3 shows that the presence of boehmite gives rise to a considerable correction to the measured amount of Al_2O_3 . Consequently the amount of Al in the final formula is sensitive to the estimated amount of boehmite. An attempt to measure the boehmite impurity directly by an X-ray method was not successful, probably because the boehmite sample used as an X-ray standard was considerably better crystalline than the boehmite in the takovite sample. Therefore greater reliance is placed on the formula derived for the Australian sample, where only kaolinite is present as an impurity.

Discussion and conclusions

This investigation is concerned primarily with establishing the identity of the mineral takovite as a member of the pyroaurite group. The principal difficulty has been in obtaining suitable samples for study, and particularly material from the type locality. A few milligrams of the material from Takovo, Serbia, established the identical nature of the X-ray powder patterns and infrared absorption spectra of the Takovo, Australia, and Var samples and proved that the type material is indeed a hydrous carbonate mineral, which was not recognized when the mineral was originally named (Maksimovic, 1957). The determination of a chemical formula is feasible only with the Australian and Var samples, both of which contain appreciable impurities. A correction for kaolinite in the Australian sample involves less uncertainty than the corrections for boehmite and lesser kaolinite in the Var sample. The final results, however, are very similar and come close to

the formula $\text{Ni}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3) \cdot 4\text{H}_2\text{O}$. Only small substitutions of Ni by Mg and of Al by Fe^{3+} are found. Also $(\text{CO}_3)^{2-}$ is probably replaced to a small extent by $2(\text{OH})^-$, and the molecular water may exceed $4\text{H}_2\text{O}$ by about 0.5–1.0 H_2O . A structure analysis of pyroaurite by Allmann (1968) indicated room for 5 molecules of H_2O in the interlayer.

Two aspects of takovite call for further study. If pure samples can be obtained, a further chemical analysis will be worthwhile. Also a structure determination will be of interest, especially if a single crystal can be obtained.

The mineral for which the name eardleyite was suggested [Fleischer (1962) commented that "names should not be published without adequate data"] appears to be a zincian form of takovite. The Ni:Zn ratio was given as 11:1, and the proportion of Zn is probably insufficient to justify a new name. On the basis of X-ray and infrared data it was recognized as being analogous to hydrotalcite (Anderson and Whelan, 1962). It might, therefore, be called a zincian takovite.

Acknowledgments

We thank Mr. Roy Hose, Dr. Z. Maksimovic, and Dr. E. H. Nickel for making samples of takovite available for this study and also Mr. G. H. Sabiston and Mr. Louis Gallay for their assistance in obtaining materials. We thank Dr. Peter Deines for assistance in determining the CO_2 content of two samples, and Mr. James Ashu for the thermogravimetric data. We are indebted to the National Science Foundation for grant GA-41413 which has supported this research.

References

- Allmann, R. (1968) The crystal structure of pyroaurite. *Acta Crystallogr.* B24, 972–977.
- (1970) Doppelschichtstrukturen mit brucitähnlichen Schichten $[\text{Me}(\text{II})_{1-x}\text{Me}(\text{III})_x(\text{OH})_2]^{x+}$. *Chimia*, 24, 99–108.
- and H. P. Jepsen (1969) Die Struktur des Hydrotalkits. *Neues Jahrb. Mineral. Monatsh.*, 544–551.
- and H. H. Lohse (1966) Die Kristallstruktur des Sjögrenits und eines Umwandlungsproduktes des Koenenits (=Chlormannasseits). *Neues Jahrb. Mineral. Monatsh.*, 161–181.
- Anderson, B. J. and J. A. Whelan (1962) Nickel-bearing minerals in the southern Oquirrh Mountains, Utah (abstr.) *Geol. Soc. Am. Spec. Pap.*, 68, 83.
- Appleman, D. E. and H. T. Evans, Jr. (1973) Job 9214: Indexing and least-squares refinement of powder diffraction data. Natl. Tech. Inf. Serv., U.S. Dept. of Commer., Springfield, Virginia, Document PB 216 188.
- Brown, G. and M. C. Gastuche (1967) Mixed magnesium–aluminum hydroxides: II Structures and structural chemistry of synthetic hydroxycarbonates and related minerals and compounds. *Clay Minerals*, 7, 193–201.
- De Waal, S. A. and E. A. Viljoen (1971) Nickel minerals from Barberton, South Africa: IV. Reevesite, a member of the hydrotalcite group. *Am. Mineral.*, 56, 1077–1081.

- Faye, G. H. (1974) Optical absorption spectrum of Ni^{2+} in garnierite: a discussion. *Can. Mineral.*, 12, 389-393.
- Fleischer, M. (1962) Eardleyite (under New Mineral Names) *Am. Mineral.*, 47, 807.
- Fron del, C. (1941) Constitution and polymorphism of the pyroaurite and sjögrenite groups. *Am. Mineral.*, 26, 295-315.
- Maksimovic, Z. (1957) Takovite, hydrous nickel aluminate, a new mineral. *C. r. geol. soc. serbe*, 1955, 219-224. (in Serbian).
- (1968) The properties and genesis of takovite. Symposium on the structure, genesis, and properties of clays and other silicate raw materials, Zagreb. 12-15.
- (1970) Features and genesis of takovite. *Zap. Vses. Mineral. Obshch.*, 99, 595-600 (in Russian).
- (1973) Nickel clay minerals in some laterites, bauxites, and oolitic iron ores. *Proc. Sixth Conf., Clay Mineral. Petrol.*, 119-134.
- Mumpton, F. A., H. W. Jaffe and C. S. Thompson (1965) Coalingite, a new mineral from the New Idria serpentinite, Fresno and San Benito counties, California. *Am. Mineral.*, 50, 1893-1913.
- Rouxhet, P. G. and H. F. W. Taylor (1969) Thermal decomposition of sjögrenite and pyroaurite. *Chimia*, 23, 480-485.
- Suhr, N. H. and C. O. Ingamells (1966) Solution technique for analysis of silicates. *Anal. Chem.*, 38, 730-734.
- Taylor, H. F. W. (1973) Crystal structures of some double hydroxide minerals. *Mineral. Mag.*, 39, 377-389.
- White, J. S., Jr., E. P. Henderson and B. Mason (1967) Secondary minerals produced by weathering of the Wolf Creek meteorite. *Am. Mineral.*, 52, 1190-1197.
- White, W. B. (1971) Infrared characterization of water and hydroxy ion in the basic magnesium carbonate minerals. *Am. Mineral.*, 56, 46-53.

Manuscript received, November 10, 1975; accepted for publication, February 2, 1977.