

NOTES

PREPARATION AND PROPERTIES OF PYROAURITE-LIKE
HYDROXY MINERALS

Key Words—Infrared spectroscopy, Pyroaurite, Sjögrenite, Synthesis, Thermal stability, X-ray powder diffraction.

INTRODUCTION

Natural and synthetic minerals of the type $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{+R}(R/n)A^{-n} \cdot mH_2O$, where $M^{2+} = Mg, Fe, Ni$; $M^{3+} = Al, Fe, Cr$; and $A = CO_3, SO_4, NO_3$; are classified as the pyroaurite-sjögrenite group. Natural pyroaurite and sjögrenite are polymorphs having the composition $Mg_6Fe_2(OH)_{16}CO_3 \cdot 4H_2O$ and crystal structures consisting of brucite-like layers $[Mg_6Fe_2(OH)_{16}]^{2+}$ intercalated with CO_3^{2-} and water molecules (Allmann, 1968). The proportion of M^{2+} to M^{3+} cations varies in minerals of this series, but in natural pyroaurite and sjögrenite it is near 3:1 (Fron del, 1941; Rouxhet and Taylor, 1969; Taylor, 1973). The ratio varies from 2:1 to 5:1 in synthetic phases similar to hydrotalcite (Gastuche *et al.*, 1967; Brindley and Kikkawa, 1979; Kikkawa and Koizumi, 1982). Taylor (1969) found two products having Mg:Fe ratios of 2:1 and 12:1 intergrown in a natural pyroaurite-sjögrenite specimen. Splitting of basal reflections was noted in natural sjögrenite (Taylor, 1969) and in synthetic hydrotalcite and were related to their difference in $M^{2+}:M^{3+}$ ratio (Gastuche *et al.*, 1967); however, no systematic study of the compositional range of pyroaurite-sjögrenite minerals has been reported.

The present study is concerned with the range of Mg:Fe ratio in synthetic pyroaurite. The effect of compositional variation on the lattice parameters, infrared spectra, and thermal behavior of these minerals has also been investigated.

EXPERIMENTAL

Mixed solutions of $MgCl_2$ and $FeCl_3$, having total cation concentrations of 0.5 M, were prepared with Mg:Fe ratios between 1.5:1 and 12:1. Twenty milliliters of the mixtures were added drop-wise with vigorous stirring into 250 ml of 0.2 M NaOH containing 10 mmoles of Na_2CO_3 as the carbonate source. The precipitates were aged in the solutions at 60°C for 10 days, washed with distilled water five times after centrifugation, and dried overnight at 80°C. All procedures were carried out in plastic vessels to avoid contamination with silica. Nitrates and sulfates also were used as starting materials, but crystallization in these systems was extremely poor.

All products were examined by X-ray powder diffraction (XRD) techniques using filtered $CoK\alpha$ radiation. The interlayer distance, c' , was determined using the 003 and 006 basal reflections. Infrared (IR) spectra were obtained by the KBr pellet technique in the region between 4000 and 200 cm^{-1} . Thermal gravimetric (TGA) and differential thermal (DTA) data were measured with a temperature increase of 10°C/min up to 800°C in air. Cation contents were determined by atomic absorption.

RESULTS

Pyroaurite-like compounds were obtained over the entire compositional range of the starting solutions. XRD patterns were indexed using hexagonal parameters, and the lattice parameters, a and c , were estimated using the 110, 003, and 006 reflections. The interlayer distance, c' , corresponding to $c/3$ (plotted against the composition x in Figure 1) changed from 7.95 Å to 7.75 Å in the composition range, $0.15 < x < 0.27$. Products in this range were pyroaurite-like compounds un-

contaminated with other phases. At $x < 0.15$, brucite, $Mg(OH)_2$, coexisted with pyroaurite, and the interlayer distance of pyroaurite was constant. The pyroaurite-like compounds formed in this range probably had a constant composition of $x = 0.15$, and excess magnesium precipitated as brucite. For systems with $x > 0.27$, the interlayer distance of the pyroaurite-like products was also constant, excess iron probably precipitated as noncrystalline $Fe(OH)_3$. Atomic absorption analysis showed that the Mg:Fe ratios of the precipitates were equal to those of the starting solutions. Thus, neither Mg nor Fe precipitated preferentially. The color of the products with $x < 0.27$ was almost white despite the presumed presence of iron. The color became dark brown for compositions with $x > 0.27$. The parameter, a , was 3.10 Å at $x = 0.25$ and decreased to 3.09 Å at $x = 0.15$ with increase in the amount of Fe. The ionic radii are 0.720 Å for Mg^{2+} and 0.645 Å for high spin Fe^{3+} (Shannon and Prewitt, 1969). Mg and Fe are located in the same layer of the structure in a hexagonal network. Thus, the substitution of Mg^{2+} with smaller Fe^{3+} decreased the a -parameter. Such a decrease in a -parameters with compositional changes was also

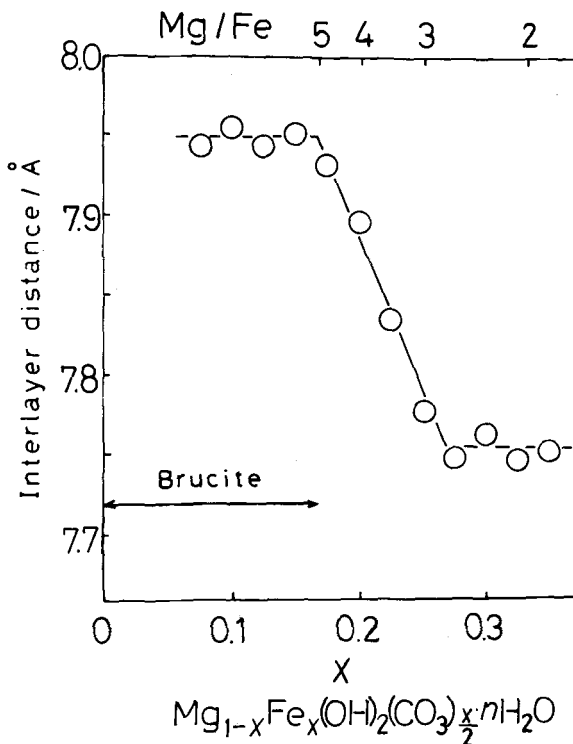


Figure 1. Interlayer distance of synthetic pyroaurite-like phases changing with composition. Product with $x < 0.15$ contained brucite as a second phase.

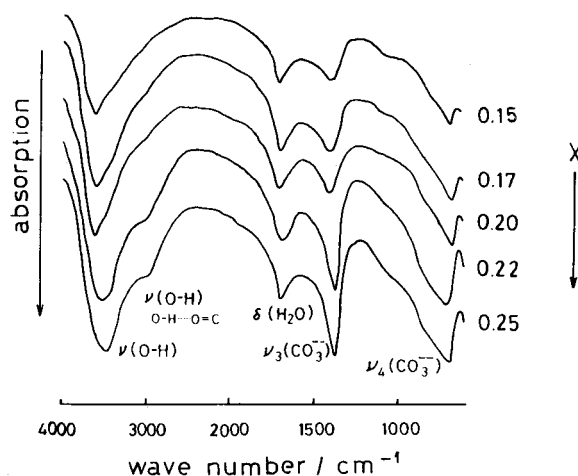


Figure 2. Infrared spectra of synthetic pyroaurite-like phases.

observed for synthetic Mg-Al and Ni-Al varieties of these minerals by Brindley and Kikkawa (1979).

IR spectra of the pyroaurite-like compounds (Figure 2) at 3600 cm^{-1} and 1650 cm^{-1} were assigned to a stretching vibration of OH and a bending vibration of H_2O , respectively. The ν_3 and ν_4 absorptions of carbonate were observed at 1360 cm^{-1} and 660 cm^{-1} . The absorption around 3000 cm^{-1} was assigned to a stretching vibration of OH bonded to carbonate (Rouxhet and Taylor, 1969). The intensity of these carbonate-related absorptions increased with the increasing x ; thus, the amount of interlayered carbonate appears to increase with an increase of positive charge in the host brucite-like layer.

The thermal decomposition of the pyroaurite-like compounds and of brucite using TGA and DTA was similar to that of natural pyroaurite (Rouxhet and Taylor, 1969); they decomposed to noncrystalline oxides by a two-step reaction as shown in Figure 3. Interlayer water was lost during the first reaction around 200°C and reversibly absorbed when the sample was quenched from just above the reaction temperature. The host brucite-like layer was not destroyed in the reaction, but CO_2 was gradually released from the interlayer region during the second reaction between about 300° and 500°C . The host layer dehydrated in the process. On the other hand, brucite itself showed no change until 380°C and dehydrated rapidly at 400°C . The carbonate in the pyroaurite-like products probably promoted the dehydration of the brucite-like layer. Reflections of MgO and MgFe_2O_4 were noted in XRD pattern of the pyroaurite heated to 800°C .

The nature of thermal decomposition changed with composition in the various pyroaurite-like compounds. As summarized in the table in Figure 3, the reaction temperature T_1 increased, whereas T_2 decreased with an increase in x . The interlayered water was retained in the compound to higher temperatures in pyroaurites having larger proportions of Fe. The host layer started to decompose with desorption of interlayered carbonate at a lower temperature in the most iron-rich compounds.

DISCUSSION

Pyroaurite-like compounds can be prepared without contamination with other phases in the compositional range of $0.15 < x < 0.27$. These compositional limits correspond to the

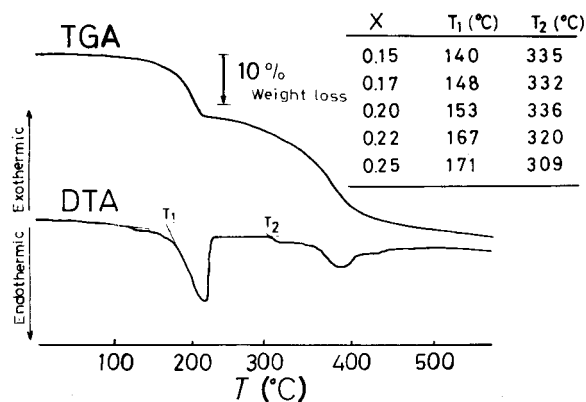


Figure 3. Thermal decomposition of synthetic pyroaurite-like phases. Compositional dependences are shown in the table.

cation ratio of Mg:Fe $\approx 5:1$ and $3:1$. Natural pyroaurite has a composition near $\text{Mg}_6\text{Fe}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$. Thus, the most iron-rich phase observed in the present study has the same Mg:Fe as natural pyroaurite. Lattice parameters for this synthetic pyroaurite are $a = 3.107\text{ \AA}$, $c = 3c' = 3 \times 7.756\text{ \AA} = 23.268\text{ \AA}$ at $x = 0.25$. These values are comparable with those of $a = 3.109\text{ \AA}$ and $c = 23.417\text{ \AA}$ for natural pyroaurite (Allmann, 1968). Taylor (1969) observed the intergrowth of regions of $\text{Mg}_{2/3}\text{Fe}_{1/3}(\text{OH})_2(\text{CO}_3)_{1/6}(\text{H}_2\text{O})_{0.4}$ and $\text{Mg}_{12/13}\text{Fe}_{1/13}(\text{OH})_2(\text{CO}_3)_{1/26}(\text{H}_2\text{O})_{0.8}$ in a natural mixture of pyroaurite and sjögrenite. These compositions are significantly different from the compositional range determined in the present study. However, what Taylor actually observed were regions having a -axial lengths of 3 and 13 times the basic value; he noted (Taylor, 1973) that these values did not necessarily imply 2:1 and 12:1 ratios, because sites could be statistically occupied. Coalingite, of approximate composition $\text{Mg}_{10}\text{Fe}_2(\text{OH})_{24}\text{CO}_3 \cdot 2\text{H}_2\text{O}$ (Mumpton *et al.*, 1965), has a structure similar to that of pyroaurite, but in this mineral two brucite-like layers occur between successive interlayers. Coalingite was not observed in the present investigation though its composition is similar to that of Mg-rich end of the present pyroaurite range. The ratio of Mg:Al in hydroxalite changes from 2:1 to 5:1 (Gastuche *et al.*, 1967; Brindley and Kikkawa, 1979; Kikkawa and Koizumi, 1982). The ratio of the trivalent cation-rich end is different from that of pyroaurite.

The layer spacing c' is a combined thickness of the host brucite-like layer and the interlayer containing carbonates and water molecules. The decrease of c' with the increase in the x ratio is attributed to the increase in the electronic attraction between the positive host layer and the negative interlayer (Gastuche *et al.*, 1967; Brindley and Kikkawa, 1979). The diffusion of water molecules in the interlayer region is depressed with the decrease of the interlayer distance, and the interlayered water begins to be released at a higher temperature in the sample having a smaller interlayer distance.

The carbonate ions are distributed in the interlayer region as far apart as possible because of their mutual repulsion. They are surrounded by water molecules, thereby reducing this repulsion. Possible arrangements of carbonate ions and water molecules were proposed for natural pyroaurite of $x = 0.25$ (Allmann, 1970). The amount of interlayered carbonate decreases with the decrease of x , and their mutual repulsion decreases with the increased distance between them. Thus, the interlayered carbonates are released from the interlayer at higher temperature in samples having less carbonate.

ACKNOWLEDGMENT

This research was partly supported by Grant-in-Aid for Developmental Scientific Research from the Ministry of Education.

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(Received 22 June 1982; accepted 10 October 1982)