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# THE NATURE AND SYNTHESIS OF FERRIMOLYBDITE

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## Abstract

The yellow coating frequently found on sulfide ores of molybdenum and described as ferrimolybdite has been studied. New data are given based on studies by *x*-ray diffraction, differential thermal analysis, optical examination, and infrared absorption. The mineral has been synthesized and the artificial product compared with natural ferrimolybdite.

## Introduction

It has long been recognized that oxidation produces a yellow coating on sulfide ores of molybdenum and early specimens in a number of collections carried the label molybdic $MoO_3$ with the belief that the coating was molybdic oxide. However, through the work of Schaller (1907), Guild (1907), Pilipenko (1914), Smith (1923), Simpson (1926) and others it has become apparent that the yellow material ordinarily observed is ferrimolybdite.

Recently, through the courtesy of the Climax Molybdenum Company a suite of oxidized molybdenum ores from Climax, Colorado was assembled. It was decided to examine the yellow oxidized mineral of these ores and compare it with similar material from other localities. It was felt to be particularly desirable to confirm the absence of molybdite, to obtain more data on the nature of ferrimolybdite, and for purposes of study to prepare synthetic material comparable to natural ferrimolybdite.

The yellow mineral of Climax is essentially microcrystalline and consists of minutely massive material, bundles of fine fibers, and nodules of radial fibers. It is found associated with limonite, goethite and jarosite in surface exposures and drill holes in the vicinity of the large caved area above the Climax mine. Presumably the weathering of pyrite and molybdenite has resulted in the formation of ferrimolybdite, and at the same time jarosite, goethite and limonite were produced, all of which yield molybdenum on analysis. The yellow mineral may occur intimately mixed with these associates, in isolated veinlets, disseminated through the oxidized material, or in thin crusts. Apparently it is one of the products of oxidation. In hand specimen ferrimolybdite may form bands around small molybdenite areas and grade into surrounding limonite.

This study has been supported by the Climax Molybdenum Co., and the courtesy of the company in releasing the paper for publication is gratefully acknowledged. We are indebted to Prof. Nathaniel Arbiter for separated concentrates of Climax minerals. The optical studies, early mineral separations and initial *x*-ray data were made with the assistance of Mr. Carl Hott.

## CHEMICAL COMPOSITION

Palache *et al.* (1951, p. 1095) give the composition of ferrimolybdite as $Fe_2(MoO_4)_3 \cdot 8\ H_2O$ ($3\ MoO_3 : Fe_2O_3 : 8\ H_2O$). The molecular proportions of these components represent averages from numerous analyses (Table 1).

TABLE 1. ANALYSES OF FERRIMOLYBDITE

| Ratio | $MoO_3$ | : | $Fe_2O_3$ | : | $H_2O$ | Analyst | Location of Sample |
|---|---|---|---|---|---|---|---|
| 1. | 3.04 | : | 1.00 | : | 7.43 | Schaller (1907) | Westmoreland, N. H. |
| 2. | 3.4 | : | 1.00 | : | 7.3 | Schaller (1907) | Telluride, Colorado |
| 3. | 3.3 | : | 1.00 | : | 8.6 | Schaller (1907) | California |
| 4. | 3.5 | : | 1.00 | : | 7.8 | Schaller (1907) | Renfew, Ontario |
| 5. | 3.09 | : | 1.00 | : | 7.06 | Guild (1907) | Santa Rita, Airzona |
| 6. | 3.14 | : | 1.00 | : | 7.11 | Guild (1907) | Santa Rita, Arizona |
| 7. | 3.90 | : | 1.00 | : | 10.00 | Simpson (1926) | Mt. Mulgine, W. Aus. |
| 8. | 3.90 | : | 1.00 | : | 9.37 | Simpson (1926) | Mt. Mulgine, W. Aus. |
| 9. | 2.86 | : | 1.00 | : | 7.42 | Smith (1923) | Wilson's Downfall, S. Wales |
| 10. | 3.26 | : | 1.00 | : | 8.81 | Schaller (1908) | Hortense, Colorado |
| 11. | 3.25 | : | 1.00 | : | 14.00 | Carrobi (1930) | Bivongi, Italy |
| 12. | 3.44 | : | 1.00 | : | 8.90 | Pilipenko (1914) | Yeniseisk, Siberia |
| 13. | 3.69 | : | 1.00 | : | ND | Jones and Milne (1954) | Climax, Colorado |
| 14. | 3.85 | : | 1.00 | : | ND | Jones and Milne (1954) | Climax, Colorado |

These analyses have been recalculated to 100 per cent after subtracting the "insolubles." The amount of extraneous material ranges between 1.67 and 24.0 per cent. Insolubles were not given for samples 7, 8 and 12.

The $Fe_2O_3 : MoO_3$ ratio ranges between the limits of 1:3 and 1:4 while the water content ranges considerably. With these ranges of values in mind, an attempt was made to determine the composition through synthesis. Synthesis was also undertaken to obtain uncontaminated material for laboratory study. Ferrimolybdite is found only in fine aggregates and pure natural material is both difficult to separate and limited in amount.

## PROPERTIES OF FERRIMOLYBDITE

Several physical properties of ferrimolybdite show a considerable range of values. A number of these have been re-determined, on both natural and synthetic materials, and compared with existing data.

Both natural and synthetic crystals of ferrimolybdite suggest orthorhombic crystallization on the basis of optical properties. Synthetic ferrimolybdite is easily crushed between the fingers and is 1–2 on Mohs' hardness scale. Synthetic crystals pressed to eliminate air yield a specific gravity value of 4.46; but the same material powdered yields a value as determined with the pycnometer of 3.06. The color of both natural and synthetic ferrimolybdite is 8.0 Y$\frac{5}{8}$ in Munsell colors; the streak is pale yellow. The luster of natural crystals ranges with occurrence, adamantine to silky when fibrous and earthy when encrusting. Synthetic ferrimolybdite tends to be earthy.

## SYNTHETIC FERRIMOLYBDITE

Carrobi claimed to have synthesized the hydrous iron-molybdenum oxide ferrimolybdite in 1930. Confirmation of the synthesis, however, was limited to comparison of an apparent similarity of chemical and optical properties between the synthetic substance and the mineral.

The original description of the apparent synthesis omits desirable information. Although the descriptions of the reagents are detailed, quantitative data are not included on the preparation procedure. Further, buffer solutions for maintenance of pH, are omitted, the times required for various reactions are not given and several other phases of the process are so vague as to require reworking. The experimental work has led to redevelopment of the entire synthesis technique. In addition, although the material Carrobi produced possessed the optical characteristics and chemical composition of ferrimolybdite, in the absence of *x*-ray data uncertainty concerning the identity of the synthetic compound exists. Confirmatory *x*-ray and physical measurements appeared desirable.

Carrobi used two solutions in his synthesis which were adapted to the present study as follows:

(A) Sodium molybdate-dihydrate, ($Na_2MoO_4 \cdot 2H_2O$), (14.0 g) was dissolved in distilled water (500 ml) and acidified by the addition of acetic acid (40 ml) to pH 3.5–4.0 as judged by the use of indicator paper.

(B) Ferric chloride, ($FeCl_3 \cdot 6H_2O$), (9.0 g) was dissolved in distilled water (50 ml).

Both solutions were prepared at room temperature, while the ensuing reaction was carried out at room temperature and under atmospheric pressure.

The molybdate solution (A) was placed in a beaker on a magnetic stirrer and the chloride solution (B) added slowly from a burette. The solution first turned deep red, and on the addition of about 48 ml of the chloride solution a yellow precipitate began to appear. The remainder of the chloride solution was then added, the system was stirred magnetically for 15 minutes, and was allowed to stand over night. The next day the system was magnetically stirred for 10 minutes, filtered with a Buchner funnel, washed with 95 per cent ethanol and the precipitate placed between filter papers to dry at room temperature. The preparation (laboratory No. 8) was a fine powder, extremely soft, and examination with the microscope revealed no signs of crystallinity. Powder patterns also failed to yield *x*-ray diffraction lines.

This procedure appeared to be basically correct and more experiments were continued along this line for several months. Variations in types of buffer solutions and methods of controlling the reaction were attempted. At the same time a portion of laboratory preparation No. 8 was immersed in distilled water and allowed to stand. On a chance reexamination of this material after a number of weeks it showed transparent crystals about 0.01 mm long. *X*-ray diffraction patterns of No. 8 (Water) were found to agree with patterns of natural ferrimolybdite.

At this point, a new preparation (No. 20) was made following the procedure previously employed for No. 8. In this case, however, in order to accelerate crystallization the material was repeatedly heated to 60° C. and allowed to cool.

In the period Oct. 30–Nov. 23, 1961 heating, stirring and cooling procedures were applied to a water preparation of No. 20 (Water). This resulted in a laboratory product which consisted of a yellow crystalline material. The material was made up of a mat of intergrown needle-like crystals, larger and more abundant than the crystals formed in preparation 8W. The *x*-ray diffraction measurements of this material agree with ferrimolybdite (Table 2).

In the preparation of 20W periods of 30 minutes to several hours of heating solutions up to 60° C., while stirring with a magnetic stirrer, alternated with periods of several hours of cooling and stagnation at room temperature. The process was repeated on 10 separate days in the period Oct. 30–Nov. 21. The solution was allowed to stand overnight without agitation and on weekends. By accident the solution was heated to 81° C. on Nov. 10 and 70° C. on Nov. 14, but the duration of the elevated temperature was short in both instances. Throughout, water was constantly added to the system in order to maintain the proper level of dilution.

## Identity of the Synthetic Material

The presence of crystallinity in synthetic preparations was detected by optical birefringence in polarized light and diffraction of *x*-rays.

Among 32 samples of synthetic preparations examined optically for evidence of crystallinity, 28 showed signs of an ordered atomic arrangement. All 28 of these samples were run either on the *x*-ray diffractometer or the powder camera. On examination of the *x*-ray patterns, not all of these samples were found to be ferrimolybdite. Some samples were tentatively identified as complex iron-molybdic acid which had crystallized.

Among the samples produced synthetically, two crystallized entirely with the optical and structural characteristics of ferrimolybdite (preparations 8W and 20W).

8W and 20W are both light-yellow powders. In plane polarized light, 8W is yellow-green. The interior of this sample does not display geometrical indications of crystals. With crossed nicols, however, small

TABLE 2. *X*-RAY DIFFRACTION DATA FOR FERRIMOLYBDITE

| Questa | | Santa Rita | | Buena Vista | | Climax (CH) | | Climax (JM) | | 8W | | 20W[1] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| d(Å) | $I/I_1$ | d(Å) | $I/I_1$ | d(Å) | $I/I_1$ | d(Å) | $I/I_1$ | d(Å) | $I/I_1$ | d(Å) | $I/I_1$ | d(Å) | $I/I_1$ |
| — | — | — | — | — | — | — | — | 9.9 | M | 9.9 | 10 | 10.0 | 10 |
| — | — | — | — | — | — | — | — | 8.8 | VS | 8.5 | 10 | — | — |
| 8.3 | 10 | 8.2 | 10 | 8.2 | 10 | 8.3 | 3 | 7.9 | M | — | — | 8.3 | 10 |
| 7.6 | 1 | 7.7 | 6 | 7.6 | 3 | 7.4 | 10 | 7.6 | MS | — | — | — | — |
| 6.81 | 6 | 6.80 | 8 | 6.80 | 10 | 6.77 | 3 | 6.3 | S | 6.75 | 9 | 6.75 | 9 |
| 6.00 | 1 | 6.02 | 2 | 6.00 | 1 | 6.00 | 2 | 5.9 | VW | 6.10 | W | 6.19 | 1 |
| — | — | — | — | — | — | — | — | — | — | 5.79 | W | 5.79 | 1 |
| — | — | 5.27 | 1 | 5.31 | 1 | — | — | — | — | 5.34 | VW | 5.34 | 3 |
| 5.08 | 1 | — | — | 5.08 | 1 | 5.06 | 1 | — | — | 5.01 | VW | — | — |
| — | — | — | — | — | — | — | — | — | — | 4.90 | 4 | 4.90 | 4 |
| — | — | 4.81 | 1 | 4.83 | 1 | — | — | — | — | 4.84 | 4 | — | — |
| 4.58 | 1 | 4.58 | 1 | 4.57 | 1 | — | — | — | — | — | — | — | — |
| — | — | — | — | — | — | — | — | — | — | 4.27 | 4 | 4.35 | 2 |
| 4.23 | 1 | 4.22 | 1 | 4.22 | 1 | — | — | — | — | — | — | 4.21 | 2 |
| 4.07 | 1 | 4.05 | 4 | 4.07 | 1 | 4.05 | 1 | — | — | 4.11 | 4 | 4.09 | 2 |
| — | — | 3.81 | 1 | 3.81 | 1 | — | — | 3.83 | W | 3.87 | 1 | 3.94 | W |
| — | — | — | — | — | — | — | — | — | — | 3.70 | 5 | 3.72 | 5 |
| 3.56 | 3 | 3.55 | 4 | 3.56 | 5 | 3.56 | 1 | 3.57 | W | 3.50 | 5 | 3.53 | 5 |
| 3.34 | 5 | 3.33 | 5 | 3.32 | 5 | 3.33 | 5 | — | — | 3.35 | 5 | 3.37 | 8 |
| 3.27 | 3 | 3.22 | 3 | 3.22 | 4 | 3.18 | 1 | 3.23 | W | 3.20 | 5 | 3.22 | 7 |
| 3.07 | 4 | 3.06 | 3 | 3.06 | 6 | 3.07 | 2 | 3.06 | MW | 3.04 | 4 | 3.06 | 6 |
| 2.99 | 1 | — | — | 2.98 | 1 | 2.98 | 1 | 2.97 | W | 2.94 | 1 | 2.94 | 3 |
| 2.90 | 1 | 2.90 | 1 | 2.91 | 2 | 2.90 | 1 | — | — | — | — | — | — |
| 2.80 | 1 | 2.81 | 1 | 2.82 | 1 | 2.80 | 1 | — | — | 2.77 | 7 | 2.79 | 5 |
| 2.71 | 3 | 2.71 | 7 | 2.70 | 7 | 2.71 | 4 | 2.67 | W | 2.67 | 2 | 2.66 | 3 |
| 2 57 | 2 | 2 56 | 2 | 2.57 | 2 | 2.56 | 1 | 2.58 | MW | 2.57 | 3 | 2.56 | 3 |
| — | — | — | — | 2.52 | 1 | 2.52 | 1 | 2.51 | VW | 2.53 | 3 | — | — |
| — | — | 2.45 | 1 | 2.45 | 1 | 2.45 | 1 | — | — | 2.47 | 2 | 2.47 | 2 |
| — | — | — | — | — | — | — | — | 2.39 | VW | 2.40 | 3 | 2.41 | 4 |
| 2.29 | 4 | 2.29 | 6 | 2.29 | 8 | 2.29 | 6 | 2.27 | W | 2.34 | 4 | 2.34 | 5 |
| — | — | — | — | — | — | — | — | 2.22 | MW | 2.25 | W | 2.24 | W |
| — | — | — | — | 2.14 | 1 | 2.14 | 1 | 2.12 | VW | 2.16 | 4 | 2.16 | 4 |
| — | — | 2.10 | 3 | 2.02 | 1 | 2.02 | 1 | — | — | 2.04 | 3 | 2.04 | 3 |
| 1.981 | 1 | — | — | — | — | 1.984 | 1 | — | — | 1.967 | W | — | — |
| — | — | — | — | 1.952 | 1 | 1.958 | 1 | — | — | — | — | 1.951 | W |
| — | — | — | — | — | — | — | — | — | — | — | — | 1.925 | 1 |
| — | — | — | — | — | — | — | — | — | — | 1.861 | VW | 1.875 | 1 |
| — | — | — | — | — | — | — | — | — | — | 1.812 | VW | — | — |
| — | — | — | — | 1.783 | 1 | 1.783 | 1 | — | — | 1.786 | W | 1.796 | 2 |
| — | — | — | — | — | — | — | — | — | — | 1.740 | W | 1.745 | 1 |
| 1.720 | 1 | 1.719 | 1 | — | — | 1.718 | 1 | — | — | — | — | 1.697 | W |
| 1.666 | 1 | 1.669 | 1 | 1.667 | 1 | 1.666 | 1 | — | — | 1.688 | 1 | 1.674 | 3 |
| 1.631 | 1 | 1.635 | 1 | 1.632 | 1 | 1.632 | 1 | — | — | 1.625 | 3 | 1.633 | 5 |
| 1.604 | 1 | 1.603 | 1 | 1.603 | 1 | 1.604 | 1 | — | — | 1.610 | 1 | 1.610 | 1 |
| — | — | — | — | — | — | — | — | — | — | — | — | 1.576 | VW |
| — | — | — | — | — | — | — | — | — | — | 1.545 | W | 1.550 | 1 |
| — | — | — | — | 1.509 | 1 | 1.509 | 1 | — | — | 1.491 | 1 | 1.493 | 1 |
| | | | | | | | | | | | | 1.470 | 1 |
| | | | | | | | | | | | | 1.438 | VW |
| | | | | | | | | | | | | 1.420 | 1 |
| | | | | | | | | | | | | 1.397 | W |
| | | | | | | | | | | | | 1.374 | W |

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[1] 20W Plus six more reflections to 2$\theta$ equal 90°

birefringent needle-shaped crystals, 0.01 mm in length, are visible within the anhedral mass. Under a magnification of 360×, these needles display birefringence of the 2nd order with extinction parallel to crystal length. Such optical features were reported by Carrobi.

Sample number 20W shows crystallinity in plane polarized light, with crystal outlines visible without the benefit of crossed nicols. Under crossed nicols, the sample appears as a mat of intergrown fibers, in a pilotaxitic relationship. The average length of these needles is 0.3 mm, with some crystals nearly 1.0 mm long. The birefringence is upper first order with extinction parallel to the length of the crystal.

The first sample to be run on the powder camera was 8W and several photos were taken. Secondary fluorescence of iron in the sample was reduced by using sheet aluminum filters, and the optimum exposure time for best reflection resolution was established. The resulting patterns show more reflections than naturally occurring ferrimolybdite (Table 2).

One powder photograph of 8W (Table 2, Column 6) revealed 38 reflections in 8.5 hours with a single sheet of aluminum foil as a filter. An *x*-ray photograph of 20W produced 49 reflections. This was taken with a double layer of aluminum foil as a filter and exposed for 7.0 hours.

Table 2 shows reflections obtained from four carefully separated ferrimolybdites; Questa, New Mexico, Santa Rita, Arizona, Buena Vista, Colorado, and Climax, Colorado. The four reference localities are included since a considerable range both in position and intensity has been observed in *x*-ray reflections of natural ferrimolybdite. Spacings at 9.9–10.0° occur in fully hydrated material, but may be otherwise absent.

No. 22W was prepared in sufficient quantity for chemical analysis following the procedure for 20W, and was analyzed by Mr. R. H. Maurer, Climax Molybdenum Corporation Detroit Laboratory as follows:

Chemical Analysis of Synthetic Ferrimolybdite (22W)

| | Original % | Recalculated to 100% |
|---|---|---|
| Total $H_2O$ | 20.94 | 20.85 |
| $Fe_2O_3$ | 17.53 | 17.45 |
| $MoO_3$ | 61.98 | 61.70 |
| Total | 100.45 | 100.00 |

Resulting molecular proportions: 1 $Fe_2O_3$:3.9 $MoO_3$:10.5 $H_2O$.

Total water was determined by loss on ignition at 500° C. This probably includes some adsorbed water and is therefore in excess of the postulated octahydrate state. The per cent of molybdic oxide per 100 per cent of sample is in general agreement with analyses from the literature while the per cent of ferric oxide is low.

The *x*-ray data for 22W agree with data for natural ferrimolybdites. The range from a molecular proportion of 1:3 $Fe_2O_3$:$MoO_3$ to a ratio of 1:4 may not radically change the structure. It is possible the Fe:Mo oxide ratio is not stoichiometric at 1:3, and may range within the limits of 1:3–1:4.

TABLE 3. OPTICAL PROPERTIES[1]

| | Larsen and Berman (1934) | | | Jones and Milne (1954) | | Carrobi (1927) | Yarosh (1955) | (1962) | |
|---|---|---|---|---|---|---|---|---|---|
| | Locations not cited | | | a) Mt. Mulgine W. Aus.<br>b) Climax, Colo. | | Bivongi, Italy | Blagodot USSR | Climax, Colo. | |
| | | | | (a) | (b) | | | | |
| $\alpha$ | 1.78 | 1.74 | 1.720 | 1.75 | 1.70 | 1.731 | 1.797 | 1.806 | 1.791 |
| $\beta$ | 1.79 | 1.75 | 1.733 | 1.79 | 1.76 | 1.731 | — | 1.827 | 1.808 |
| $\gamma$ | 2.04 | 1.95 | 1.935 | 1.89 | 1.85 | 1.740 | 1.980 | 2.005 | 1.997 |
| 2V | small | small | 28° | small | — | — | — | — | — |
| Sign | pos. | pos. | pos. | pos. | — | — | — | pos. | pos. |

Palache *et al.* (1951) have suggested that the range in the indices of refraction is caused by differences in water content. Present chemical analyses show possible ranges in Mo:Fe ratio which may also alter optical properties. Natural ferrimolybdite crystals from Climax exhibit the following optical characteristics.

Pleochroism: X and Y clear. Z ash-gray to canary-yellow or olive-green. r<v Crystals are length slow (Z), with Z as the direction of elongation. Absorption is strongest parallel to Z. Extinction is parallel.

[1] The above optical properties for natural ferrimolybdite from Climax, Colorado were determined by Mr. Carl Hott.

## DIFFERENTIAL THERMAL ANALYSIS

Both Schaller (1907) and Carrobi (1930) made dehydration studies of ferrimolybdite as follows:

| Temperature ° C. | Schaller Remaining $H_2O$ (1907) | Carrobi Remaining $H_2O$ (1930) |
|---|---|---|
| 25 | 7.5 | 8.0 |
| 78 | not determined | 4.0 |
| 110 | 1.5 | 3.0 |
| 125 | 1.0 | not determined |
| 180–185 | 0.5 | 2.1 |
| 200 | less 0.5 | 1.0 |
| 250 | not determined | less 1.0 |

The two studies are basically similar, Up to one-half the water of crystallization is lost at temperatures between 25° C. and 78° C. At a temperature of 110° C., the "normal" temperature for driving off non-structural water, the structure is nearly dehydrated. The mineral may be further dehydrated in the temperature range 200–250° C., where it apparently becomes anhydrous.

Golding *et al.* (1960) found that ferrimolybdite dehydrated at temperatures as low as 50° C. In the current study the thermal history of ferrimolybdite was examined by differential thermal analysis (DTA). The reactions on the curve for natural ferrimolybdite from Buena Vista, Colorado, (Fig. 1) are tabulated at the top of the next page.

The *x*-ray data are shown in Table 4. In general, the above reactions fit the dehydration data described by Schaller and Carrobi. The first endothermic peak at 40° C. may be questionable, but it agrees approximately with the observations of Golding, *et al.* (1960). The amount of dehydration is probably small, since the physical characteristics, color and the *x*-ray pattern, of the 65° C. product and the natural unheated material are quite similar.

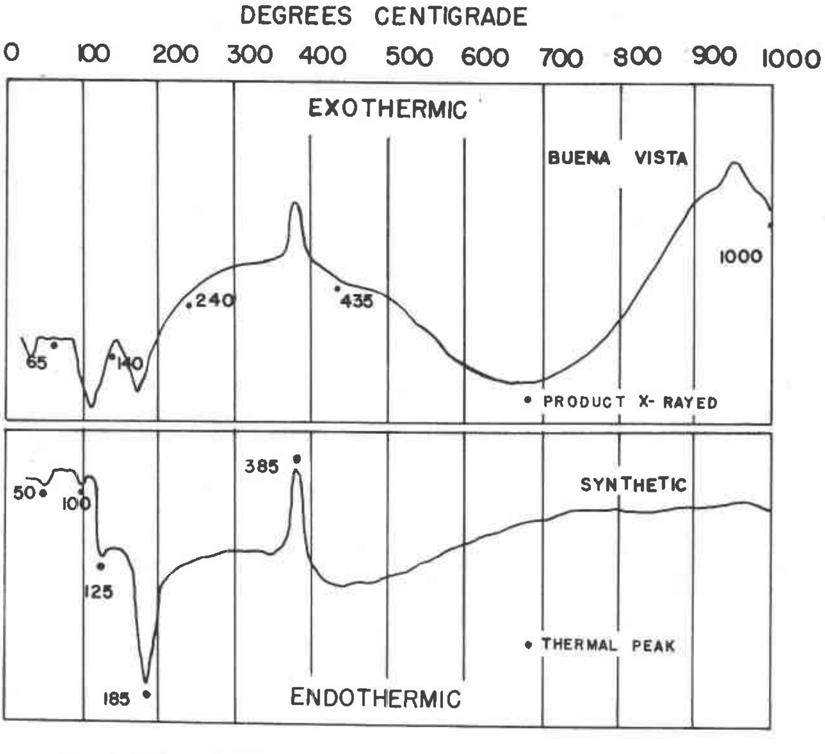

FIG. 1. Differential thermal curves of natural and synthetic ferrimolybdite.

| Reaction | Start (T° C.) | Peak (T° C.) | Products by $x$-rays | No. of Reflections | Color |
|---|---|---|---|---|---|
| | | | Natural ferrimolybdite | 58 | Yellow |
| Endothermic | 30 | 40 | 65 | 65 | Yellow |
| Endothermic | 90[1] | 110 | 140 | 58 | Yellow-green |
| Endothermic | 150[1] | 165 | 240 | 51 | Dull-yellow green |
| Exothermic | 365[1] | 375 | 435 | 57 | Dull-gray green |
| Exothermic | 950 | 960 | 1040 | 71 | Dark-gray green |

[1] Indicates a first order reaction.

The material produced at 140° C., above the 110° endothermic peak, resembles the 65° C. material structurally, but color indicates a physical change.

The dehydration peak at 165° C. represents a major structural change, as shown by a pronounced change in color as well as the $x$-ray pattern of the material formed 240° C. At this temperature, the normal base-line is regained after the reaction. The physical changes support the dehydration data and indicate the formation of the anhydrous ferrimolybdite phase in this temperature range.

At 365° C. a new structural phase is developed. The material resembles physically that formed above the dehydration peak at 165° C., but in the higher temperature product, the lines are more numerous and intense, indicating complete removal of residual water and the formation of Fe-Mo oxide.

The material formed at 1040° C. is similar in structure and color to the 435° C. material, but new reflections appear in the smaller d-spacing area. This is probably the end-product of the dehydrated material.

Figure 1 represents the differential thermal curve for synthetic ferrimolybdite No. 22W. The reaction types and temperature ranges are similar to the natural material. Reactions 2 and 3 centered at 110° C. for the synthetic material, were recorded as a single reaction in the natural material. Since this sample shows abundant fine-grained, pure material, which would yield a sensitive reaction, this curve probably represents the actual dehydration. The major peaks at 185° C. and 385° C. are slightly higher than for the natural material, but the overall comparison is satisfactory. It should also be noted that the dehydration of the synthetic material begins at 50° C., as described in the literature.

## INFRARED SPECTROSCOPY

Infrared curves were run to ascertain the type or types of water bonding in ferrimolybdite, the effect of increasing temperatures on the rate of water loss from the structure, and the ultimate effect of increased temperature on the ferrimolybdite structure.

The instrument used was a Pekin-Elmer Model 21 Split-Beam Infrared Spectrophotometer with a NaCl prism (Wright and Herscher, 1947). Recordings were made at the following settings: resolution 927, gain 5.5, speed 5.5 and pen speed 11.00. All phases were solid. The running time for each curve was approximately 15 minutes. The ferrimolybdite used for DTA and the products formed at 65,° 140°, 240°, 435° and 1045° C. were used for infrared curves. The preparation of samples followed procedures as outlined by Geise (1961).

## RANGES OF ABSORPTION OF WATER MOLECULES

Absorption of infrared radiation at specific wavelengths by bonded water molecules, $H_2O$, and the unbonded hydroxyl groups, (OH), yield spectral bands which have been studied extensively by organic chemists (Hunt *et al.*, 1959), and the positions of these absorption peaks on infrared spectrographs are well known. Hydroxyl groups, (OH), may absorb anywhere in the wavelength interval 2.7 to 3.1 microns. The degree of hydrogen bonding of hydroxyl groups with each other, with other oxygen atoms in the structure, structural complexity, and (OH) orientation are important factors which determine the peak position. Absorption of independent (OH) groups, monomeric groups, are in the theoretically calculated 2.75 micron area. Increase of hydrogen atoms sharing between adjacent structural oxygen atoms, or from oxygen atoms from other (OH) groups produces an absorption in the 2.85 micron area. These are dimeric groups. If adjacent (OH) groups share a hydrogen atom they absorb radiation at 2.95 microns. These are polymeric groups. (Keller and Pickett, 1949, p. 861).

Water, $H_2O$, absorbs strongly in the 3.0 micron area, less strongly in 4.5 micron area, and again strongly in the 6.0 to 6.2 micron area. Hydroxyl peaks in the 3.0 micron area are narrow and well defined, whereas the $H_2O$ peaks are broad and cover a much greater area. The 9.0 to 15.5 micron region of the infrared spectrographs is a reflection of the iron and molybdenum oxide adsorption. Data appear to be lacking in the literature concerning the importance of metallic oxide spectra of this type. However, qualitative deductions indicate that in crystals containing complex molecules, the internal vibrations caused by the heat from the infrared radiation are characteristic of the molecules involved.

Three separate determinations of the natural ferrimolybdite infrared spectrum were made to confirm the reproducibility of a single sample on successive determinations. The ferrimolybdite spectra in this micron range and the large absorption peak indicate $H_2O$ in the mineral. A slight shift off the 2.97 micron water maximum results because of the

TABLE 4. *X*-RAY DATA FOR FERRIMOLYBDITE AND DTA PRODUCTS

| Ferrimolybdite | 65° Product | 140° Product | 240° Product | 435° Product | 1050° Product |
|---|---|---|---|---|---|
| 9.93 | 10.30 | 10.04 | 10.27 | | |
| | | | 9.60 | | 9.40 |
| | | 9.11 | | | |
| 8.26 | 8.26 | 8.26 | | | |
| | 8.04 | | 8.03 | 8.04 | 7.96 |
| 7.69 | 7.69 | 7.76 | | | |
| | | | | | 7.08 |
| | | | | 6.91 | |
| 6.86 | 6.86 | 6.86 | | | |
| | | | | 6.46 | 6.46 |
| | 6.37 | | | 6.41 | |
| 6.06 | 6.15 | 6.10 | 6.19 | | |
| | | | | 5.86 | 5.82 |
| 5.30 | 5.36 | 5.30 | | | |
| 5.12 | 5.10 | 5.15 | | 5.15 | |
| | | | | 4.95 | 5.03 |
| 4.87 | | 4.84 | | | |
| | 4.79 | | | | |
| 4.62 | 4.62 | 4.62 | 4.62 | 4.62 | 4.57 |
| | 4.44 | | | 4.41 | |
| 4.25 | 4.27 | 4.27 | 4.25 | | 4.31 |
| | 4.21 | | | | |
| | | | | 4.15 | |
| 4.07 | 4.07 | 4.09 | | | 4.07 |
| | 4.00 | 4.00 | 3.98 | 3.97 | |
| | 3.91 | | | 3.90 | 3.88 |
| 3.83 | 3.81 | 3.83 | | | |
| 3.75 | 3.75 | 3.77 | 3.75 | 3.77 | 3.72 |
| 3.56 | 3.57 | 3.56 | | 3.60 | 3.54 |
| | 3.49 | | 3.49 | 2.49 | 3.45 |
| 3.44 | 3.44 | | | | |
| 3.34 | 3.35 | 3.36 | 3.36 | 3.36 | 3.31 |
| 3.24 | 3.26 | 3.28 | 3.24 | 3.28 | 3.24 |
| | | | | 3.20 | 3.19 |
| 3.07 | 3.07 | 3.06 | 3.11 | 3.09 | |
| 3.01 | 3.01 | | 3.01 | 2.99 | |
| | | | | | 2.95 |

TABLE 4.—(*Continued*)

| Ferrimolybdite | 65° Product | 140° Product | 240° Product | 435° Product | 1040° Product |
|---|---|---|---|---|---|
| 2.91 | 2.91 | | | 2.92 | |
| 2.86 | 2.87 | 2.87 | 2.86 | 2.87 | 2.86 |
| | 2.81 | 2.80 | | | 2.83 |
| 2.72 | 2.71 | 2.71 | | 2.66 | 2.68 |
| 2.58 | 2.58 | 2.59 | 2.56 | 2.58 | 2.63 |
| 2.52 | 2.53 | 2.53 | 2.51 | 2.53 | 2.51 |
| | 2.46 | 2.47 | 2.45 | 2.47 | |
| 2.40 | 2.39 | 2.42 | 2.37 | 2.41 | 2.39 |
| 2.34 | 2.34 | 2.39 | | | |
| 2.30 | 2.30 | 2.30 | 2.30 | 2.31 | 2.31 |
| | 2.29 | | | | |
| | | 2.25 | | | 2.24 |
| 2.17 | 2.21 | 2.21 | 2.20 | 2.22 | 2.20 |
| 2.15 | 2.16 | 2.15 | 2.14 | 2.14 | 2.17 |
| | 2.12 | | 2.12 | | 2.13 |
| 2.07 | 2.07 | 2.07 | 2.05 | 2.04 | 2.09 |
| 2.03 | 2.03 | 2.00 | | | 2.00 |
| 1.992 | 1.996 | | 1.988 | 1.984 | |
| 1.959 | 1.963 | 1.955 | | | 1.955 |
| | | 1.924 | | 1.932 | 1.928 |
| 1.909 | | | | | |
| | | | | 1.897 | 1.886 |
| | | 1.861 | 1.861 | | 1.868 |
| 1.840 | 1.836 | 1.830 | | 1.826 | 1.839 |
| | 1.816 | | | | |
| 1.796 | 1.789 | 1.796 | 1.796 | 1.792 | 1.802 |
| 1.754 | | 1.763 | | | 1.760 |
| 1.735 | 1.742 | 1.745 | 1.742 | 1.738 | 1.745 |
| 1.714 | 1.711 | 1.714 | 1.708 | | 1.717 |
| | | | | 1.700 | |
| 1.688 | | | | | 1.688 |
| | 1.668 | 1.671 | | | 1.665 |
| | 1.660 | | | 1.660 | 1.652 |

TABLE 4.—(*Continued*)

| Ferrimolybdite | 65° Product | 140° Product | 240° Product | 435° Product | 1040° Product |
|---|---|---|---|---|---|
| 1.633 | 1.630 | 1.633 | 1.627 | 1.633 | 1.630 |
| 1.604 | 1.600 |  | 1.594 | 1.599 | 1.596 |
| 1.577 | 1.570 | 1.579 | 1.569 | 1.576 | 1.566 |
|  | 1.550 | 1.559 |  |  |  |
|  |  |  |  | 1.541 | 1.548 |
| 1.534 | 1.527 | 1.535 | 1.529 |  | 1.434 |
|  |  |  |  |  | 1.524 |
| 1.513 | 1.513 | 1.515 | 1.511 | 1.511 |  |
|  |  |  |  | 1.493 |  |
|  |  |  |  |  | 1.483 |
| 1.470 |  |  |  |  |  |
|  | 1.456 | 1.460 | 1.458 | 1.456 | 1.454 |
| 1.436 | 1.432 | 1.434 | 1.432 | 1.432 | 1.434 |
|  |  |  | 1.412 |  | 1.414 |
| 1.399 |  |  |  |  | 1.394 |
|  |  |  |  | 1.385 |  |
| 1.379 |  |  |  |  |  |
| 1.367 | 1.367 |  | 1.370 | 1.372 | 1.365 |
|  |  |  |  |  | 1.353 |
|  |  |  |  |  | 1.338 |
|  |  |  |  |  | 1.320 |
| 1.300 |  |  |  | 1.301 | 1.301 |
| 1.280 | 1.277 | 1.278 | 1.277 | 1.277 | 1.284 |
| 1.264 | 1.262 | 1.264 | 1.262 | 1.261 | 1.264 |
| 1.253 |  | 1.251 | 1.245 | 1.244 | 1.240 |
|  |  |  | 1.233 | 1.223 |  |
|  | 1.215 |  | 1.215 |  |  |
| 1.206 | 1.203 | 1.206 | 1.205 | 1.203 | 1.207 |
|  |  |  | 1.90 |  | 1.911 |
| 1.178 |  | 1.184 | 1.180 | 1.174 |  |
|  |  |  | 1.168 |  | 1.162 |
| 1.153 |  | 1.152 | 1.151 |  | 1.153 |
|  |  | 1.140 | 1.140 | 1.145 | 1.140 |
|  |  | 1.129 |  |  |  |
| 1.118 | 1.116 | 1.117 | 1.118 |  | 1.119 |
|  |  |  | 1.105 |  | 1.103 |
|  |  |  | 1.084 |  | 1.076 |
|  |  |  |  |  | 1.064 |
|  |  |  |  |  | 1.052 |

effect of cation attraction and the water molecule in the structure; Neda and Roy (1956 p. 931) have shown that the water molecule may be broadly centered around the 3.0 micron region rather than being contained at a single wavelength (Fig. 2).

A secondary water peak, centered at 6.2 microns, is a harmonic function of the primary peak. Its presence confirms the indentification of $H_2O$. Small water peaks are also present in the 4.5 micron area.

Spectrum number 4, of the 65° C. DTA product, has a water absorption peak at 3.0 microns which has diminished in amplitude from the unheated material. A decrease in peak area is also evident. A similar change is observed in the harmonic peak in the 6 micron area. Loss of water from the structure is apparent since identical sample sizes were used.

Spectrum number 5, of the 140° C. DTA product, is similar to number 4. A slight increase in primary peak area may be caused by an increase in sample, but the harmonic peak at 6.2 microns is identical. Loss of water, as contrasted to the original mineral, is evident.

Spectra 6, 7, 8, indicate complete dehydration. The small primary water peaks are attributed to adsorbed water in the sample and the KBr matrix. Both the negligible harmonic peak, and the uniformity of the primary peaks in these spectra, indicate the presence of adsorbed water independent of mineral structure.

Samples are marked as in Fig. 2. Absorption spectra for the 7.0–9.0 micron wavelength region have been eliminated because of the absence of absorption reactions. The "pip" at 10 microns is an internal checkpoint for the spectrophotometer.

The first three spectra represent unheated ferrimolybdite. Absorption peaks are located at 10.85, 11.80, 12.46, and 13.50 microns (Table 5).

Spectrum 4 displays a change in the absorption characteristics from unheated ferrimolybdite. Broad, ill-defined, maxima are discernible in the 10.85 and 12.40 micron areas.

Spectrum 5 displays an absorption pattern which corresponds to the preceding sample 4, but shows better definition at 10.85 and 12.40 microns.

Spectra represented by curves 6, 7, 8, indicate the evolution of a new absorption pattern. The pattern comprises a change from a series of peaks distributed in the upper micron interval, to a single, well-defined trough in the 11.5–12.0 micron area. The highest temperature sample displays evidence of a split of the single peak into two peaks. The initial change to the new absorption pattern occurs in the material heated to 240° C., but the structural development is not completed until the 435° C. sample.

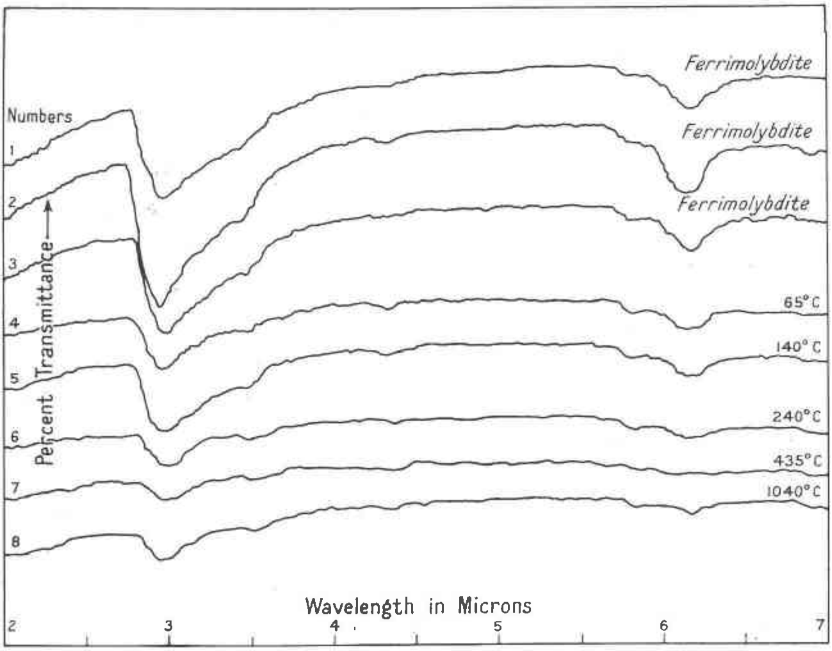

FIG. 2. Infrared spectra of ferrimolybdite and DTA products (2.0–7.0 micron area).

TABLE 5. INFRARED ABSORPTION MAXIMA OF FERRIMOLYBDITE 2–15 MICRON WAVELENGTH

| Number | Location of Maxima for Figs. 2 and 3 | | | | | |
|---|---|---|---|---|---|---|
| 1 | 2.99 | 6.20 | 10.85 | | 12.46 | 13.42 |
| 2 | 2.97 | 6.18 | 10.85 | 11.87±.1 | 12.45 | 13.45 |
| 3 | 3.05 | 6.24 | 10.91 | 11.87 | 12.45±.2 | 13.50 |
| 4 | 2.97 | 6.18 | 11.00±.1 | | 12.35±.1 | |
| 5 | 2.97 | 6.17 | 10.90±.1 | | | |
| 6 | 2.97 | 6.17 | | 12.13 | | |
| 7 | 2.97 | | | 11.85 | | |
| 8 | 2.96 | 6.16 | | 11.93 | | |
| | Location of Maxima for Fig. 4 | | | | | |
| | | | 10.85 | | | 13.42 |
| | | | 10.90 | | | |
| | | | 11.17±.1 | | 12.30±.1 | |
| | | | | | | |
| | | | | 12.10±.1 | | |
| | | | | 11.87 | | |
| | | | | 11.95 | | |

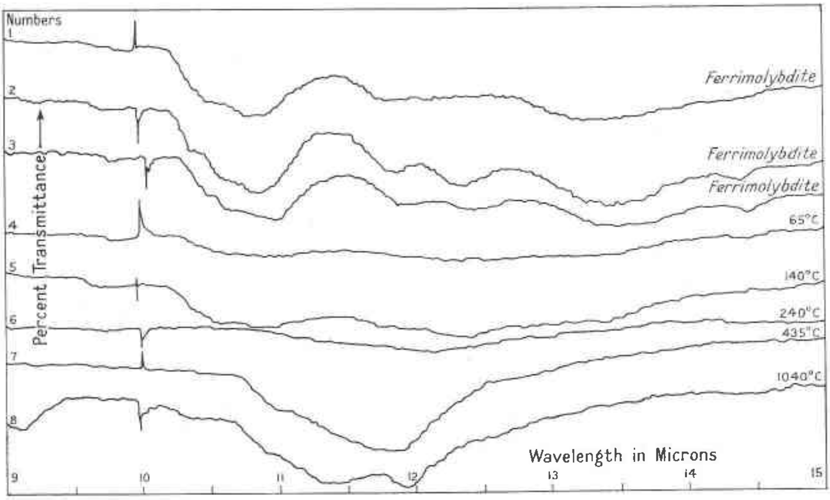

FIG. 3. Infrared spectra of ferrimolybdite and DTA products (9.0–15.0 micron area).

This was done in order to determine whether the 240° material represents a structural change into an anhydrous phase. Figure 4 resulted when the materials were treated with acetone to remove traces of adsorbed water.

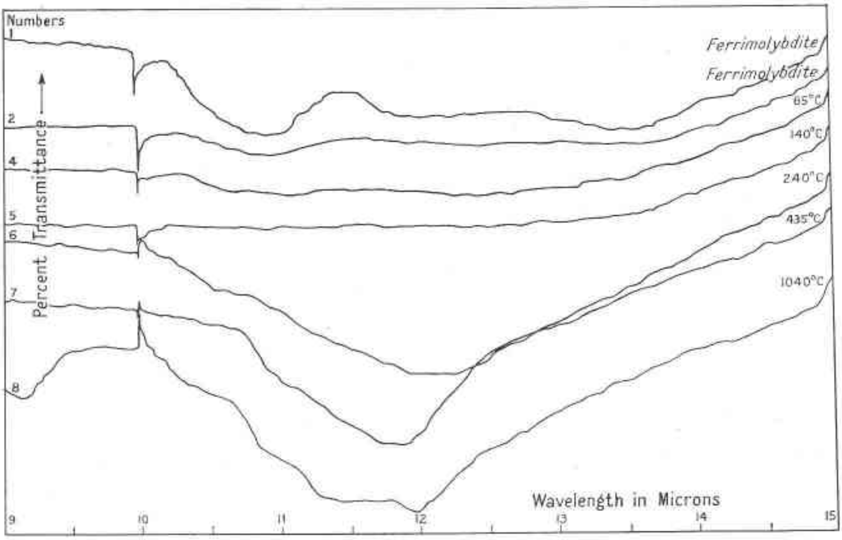

FIG. 4. Infrared spectra of ferrimolybdite and DTA products (9.0–15.0 micron area, acetone treated).

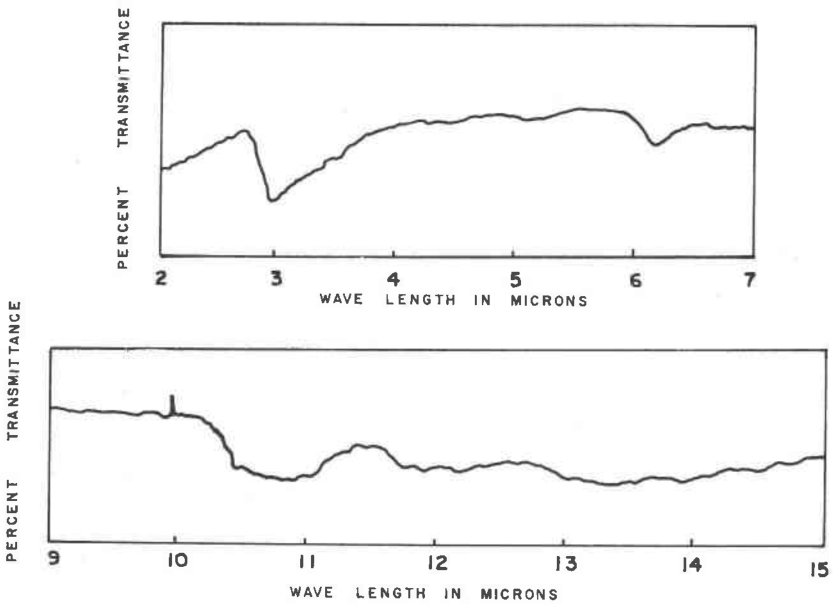

FIG. 5. Infrared absorption of synthetic ferrimolybdite.

Only two of the ferrimolybdite patterns are shown. The 240° material shows the effects of dehydration. The 240° product is structurally like the dehydrated material.

Figure 5 shows infrared spectra of synthetic ferrimolybdite No. 22W. In all aspects it is like the natural material.

## SUMMARY AND CONCLUSIONS

A study of the literature reveals a range in chemical composition, physical and optical properties of ferrimolybdite. Examination of the *x*-ray patterns reflects these differences. It has been suggested that a range in water content may in part account for these discrepencies. Recent Australian workers have found that ferrimolybdite dehydrates at relatively low temperatures on the order of 50° C., temperatures which may occasionally prevail in desert occurrences.

The synthesis of ferrimolybdite has been substantiated by *x*-ray, chemical, and physical comparison with the natural mineral. An apparent critical factor in synthesis is to allow the preparation to remain immersed in water, with occasional heating and agitation, to permit the compound to hydrate fully. Temperatures above 60° C. appeared to reduce the crystallization rate. A comparison of crystal size and abundance in laboratory preparations revealed that lower temperature solutions produced the most abundant and largest crystals.

Differential thermal analysis of natural ferrimolybdite has shown it to begin to dehydrate at temperatures as low as 50° C. A major dehydration peak begins as low as 90° C. Synthetic ferrimolybdite dehydrates at 50° C.

Synthesis of fully hydrated ferrimolybdite under conditions of atmospheric temperature and pressure indicates stability in a supergene environment. The distribution, mineral association and occurrence of ferrimolybdite at Climax, Colorado support this origin.

It is proposed that the formula $Fe_2(MoO_4)3\cdot nH_2O$ be used until a stable hydrated phase of ferrimolybdite is better established. The low temperature of stability, and the ability to dehydrate and rehydrate at 50° C., casts some doubt as to whether a low temperature phase actually exists. Furthermore, a range in Mo/Fe ratio between the limits of 1:3 and 1:4 is probable, so that the empirical formula may further change.

The water in ferrimolybdite is bonded as $H_2O$. The existence of the OH group has not been detected, but its existence in the structure is possible, in which case the absorption peaks would be included in the 3.0 micron area. The hydroxyl bonding would necessarily be dimeric or polymeric. Monomeric groups would have been detected as a separate absorption.

The progressive heating of ferrimolybdite which produces a dehydrated structure may be traced by comparison of a series of infrared spectra. The dehydration of ferrimolybdite in the 40–50° C. range is reflected in the infrared spectrum of material heated to 65° C. Completely dehydrated material results on heating to 240° C., as shown by the high wavelength absorption and by the diminished harmonic water peaks. This change in the higher wavelength area may be caused by a redistribution of the bonding charges after water is removed from the structure. Increased bonding of silicon cations and oxygen anions from nesosilicate to tektosilicate structure produces an effect whereby the absorption of radiation evolves from a series of peaks in the higher micron range, to a narrow, well-defined, single maximum in the moderate micron range (Launer, 1952). This may be anaolgous to the ferrimolybdite transformation when dehydration is completed.

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