X-RAY DIFFRACTOMETER STUDIES OF SOME VANADIUM SILICATES

By John C. Hathaway

Trace Elements Investigations Report 542

UNITED STATES DEPARTMENT OF THE INTERIOR
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IN REPLY REFER TO:

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WASHINGTON 25, D. C.

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October 26, 1955

Mr. Robert D. Nininger, Assistant Director
Division of Raw Materials
U. S. Atomic Energy Commission
Washington 25, D. C.

Dear Bob:

Transmitted herewith are three copies of TEI-542, "X-ray diffractometer studies of some vanadium silicates," by John C. Hathaway. This report was prepared entirely on Geological Survey funds, but we are transmitting it to you because we believe that it will be of interest to geologists and mineralogists working on the Atomic Energy Commission program.

We plan to publish this report in the proceedings of the National Clay Conference.

Sincerely yours,

John H. Eric
for W. H. Bradley
Chief Geologist

Geology and Mineralogy

This document consists of 21 pages.
Series A.

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

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By John C. Hathaway

ABSTRACT

A group of claylike silicates containing vanadium have been examined by X-ray diffraction methods to determine their mineralogic composition. The results indicate that mica and chlorite are the principal minerals. The micas resemble roscoelite but depart from it in two different ways: by interstratification with montmorillonitic layers and by variation in octahedral substitution. Some of the chlorites also exhibit mixed-layered expanding structures, but no interstratification of mica and chlorite layers has yet been noted. The chlorites show some variation in the temperature of decomposition, presumably because of differences in composition and degree of crystallinity.

INTRODUCTION

Identification of the claylike materials occurring in zones of vanadium mineralization in the sandstone type deposits of the Colorado Plateaus is often hampered by the fine particle size and poor crystallinity of these materials, although mica-type minerals have been recognized through usual X-ray diffraction methods and have been variously reported as roscoelite or vanadium hydromica. In this investigation, X-ray diffraction procedures commonly used in the study of clay minerals have been applied to the problem of differentiating these poorly crystalline materials.

Materials

The samples studied were as follows:

AMNH 13565, roscoelite, Coloma, California

ALB-34-54, roscoelite, Fall Creek mine, Placerville, Colorado

AW-207-54A, vanadium silicate from oxidized ore, Rifle, Colorado

AW-207-54B, vanadium silicate from unoxidized ore, Rifle, Colorado

AW-146-52, vanadium silicate from Cougar mine, San Miguel County, Colorado

AW-144-52, vanadium silicate from Sunnyside mine, east of Carrizo Mountains, San Juan County, New Mexico

AW-67-51, vanadium silicate, Little Pittsburg No. 5 mine, Thompson district, Grand County, Utah

G-53-53, vanadium silicate, Bitter Creek mine, Montrose County, Colorado

P-1-M-53, Mineral Joe mine, Jo Dandy group, Paradox Valley, Montrose County, Colorado

P-1-P-53, Mineral Joe mine, Jo Dandy group, Paradox Valley, Montrose County, Colorado

Procedure

All of the samples except AMNH 13565, P-1-M-53, and P-1-P-53 had previously been purified by water elutriation, bromoform separation, or both. Sample AMNH 13565 consisted of a group of fairly pure roscoelite crystals and therefore did not require further separation. A portion of these crystals was crushed in a mullite mortar to pass a 230-mesh sieve. This material as well as a portion of each of the other purified samples were placed in plastic test tubes and dispersed in distilled water using a motor-driven brush. A small amount of sodium metaphosphate was added to each sample as a dispersing agent.

Oriented aggregates were prepared by pipetting portions of each suspension onto each of three glass slides. The suspension remaining in the test tube was allowed to stand about four hours and the material still in suspension at the end of this time was pipetted on three additional slides. The material placed on these two groups of slides will hereinafter be referred to as coarse and fine, respectively.

Samples P-1-M-53 and P-1-P-53 were dispersed in distilled water, wet sieved to remove particles larger than 62μ, further dispersed using an end-over-end shaker, and centrifuged repeatedly to separate the silt (2-62μ) and clay (<2μ) fractions. Excess water was removed from the clay fraction using porcelain filter candles under vacuum and portions of the resulting concentrated suspensions were pipetted onto glass slides. The remaining suspensions were dried at room temperature and the clay removed and crushed.

X-ray diffractometer patterns were made for each sample as follows:

Oriented aggregates

1. Untreated
2. Treated with ethylene glycol
3. Heated to 400° C
4. Heated to 500° C
5. Treated with hot concentrated HCl (samples AMNH 13565, AW-67-51, G-53-53, P-1-M-53, and P-1-P-53 only)

Randomly oriented powder (samples AMNH 13565, ALB-34-54, P-1-M-53, and P-1-P-53, only)

Results

In figure 1 a comparison is shown between the X-ray diffractometer patterns of minerals which have been identified by chemical and optical

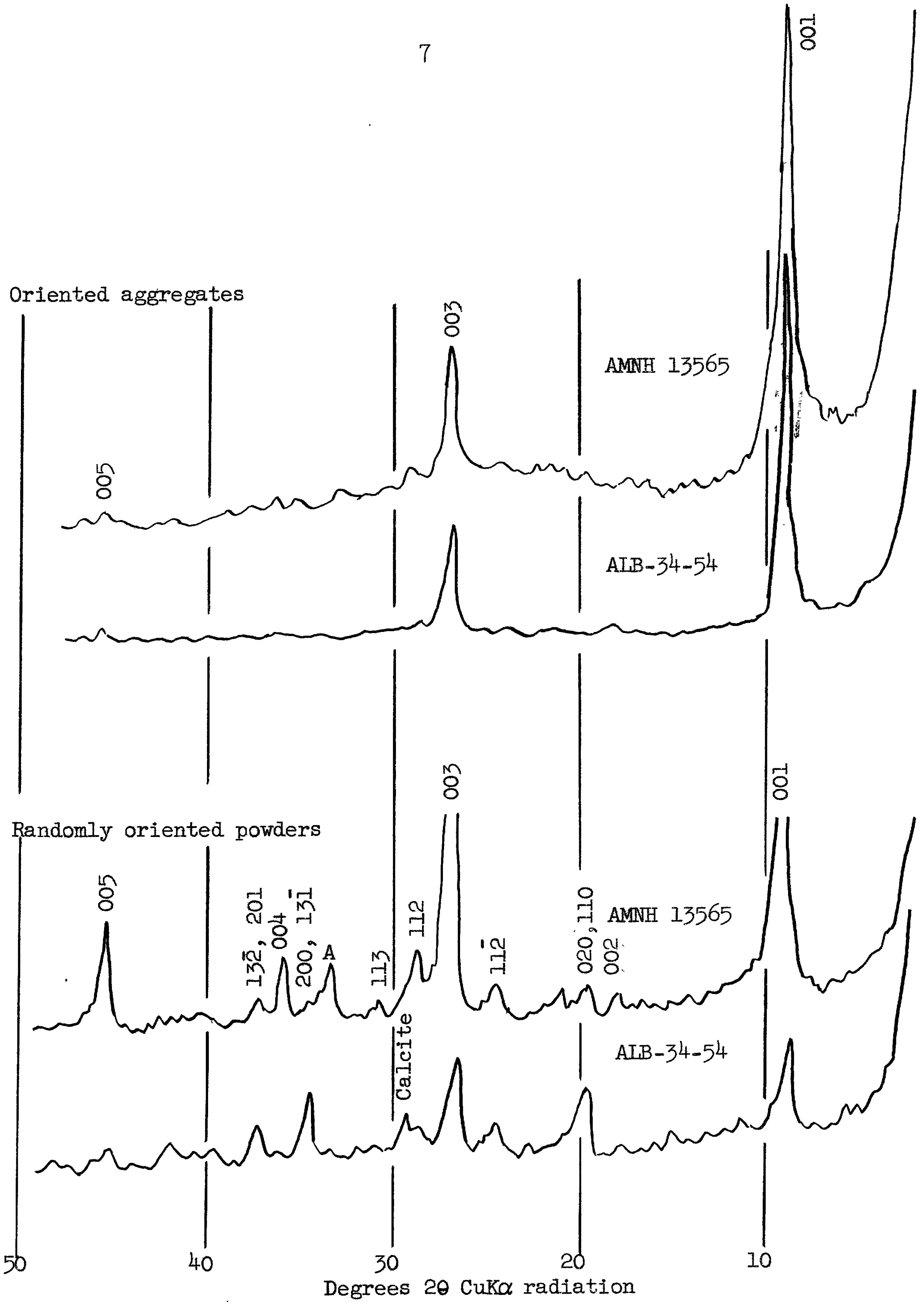

Figure 1.--X-ray diffraction patterns of two roscoelite samples.

methods as roscoelite. Most of the apparent differences in the randomly oriented powder patterns are the result of the much higher degree of preferred orientation that occurred in the preparation of the mount for sample AMNH 13565. Otherwise both samples exhibit similar patterns except that the peak marked "A" at 33.4° 2θ in the randomly oriented powder pattern for sample AMNH 13565 is not evident in ALB-34-54 and calcite is present in ALB-34-54. Inasmuch as the spacing of peak "A" is not part of the integral series of higher orders for the 001 spacing, its presence is probably not due to the preferred orientation of the roscoelite flakes but more probably represents a separate unidentified phase. Further evidence for this suggestion is the appearance of a peak with a spacing of 6.9A in the pattern for an oriented aggregate of sample AMNH 13565 heated to 500° C. The same peak appears with considerable intensity at the same temperature in the acid-treated sample suggesting that this separate phase is acid insoluble. Elimination of lines apparently due to separate phases leaves a pattern with a distribution of hkl lines that closely resembles a one-layer monoclinic muscovite. This is in agreement with the proposal of Heinrich and coworkers (1953) that roscoelite is characterized by a one-layer monoclinic structure. An important departure from the muscovite pattern may be seen in the distribution of intensities of the 00ℓ lines shown in the oriented aggregate patterns in figure 1. Whereas the 001 and 003 reflections show strong and medium intensities, respectively, the 002 and 004 reflections are almost absent. Muscovites, on the other hand, show a second-order reflection of considerably greater intensity relative to the first- and third-order reflection. A weak second-order basal reflection is usually, but not always, a characteristic of the biotites. The spacings of the 060 reflections (not shown in figure 1) for samples AMNH 13565 and ALB-34-54 are 1.525 A and 1.515 A, respectively, which places them within the overlap of the ranges usually associated with the dioctahedral and trioctahedral micas. It does not seem likely, however, that a trioctahedral mica would form with vanadium occupying the octahedral positions. Calculations of the octahedral layer population by the Marshall method (1949, p. 58) for ALB-34-54 and for a roscoelite from Placerville, Colo., from the analysis quoted in Weeks and Thompson (1954, p. 55) give sums of 1.969 and 2.069 atoms per half unit cell, respectively. It seems probable then that these micas are dioctahedral and that the moderately large b_o dimensions shown by the 060 spacings are due to the replacement of aluminum by vanadium in the octahedral layer. Such substitutions would also account for the low intensities of the second order 00ℓ reflections. G. Brown (1951, p. 162) has calculated the effect on 00ℓ intensities of substitution of Fe^{+3} for Al^{+3} in the dioctahedral mica structure and has demonstrated that a high iron mica should exhibit an extremely weak 002 reflection. As the atomic scattering curve for vanadium closely follows that of iron (Klug and Alexander, 1954, p. 138), a similar distribution of 00ℓ intensities should occur for both a roscoelite and a high iron dioctahedral mica such as a glauconite, and figure 2 shows the similarity of the X-ray patterns for oriented aggregates of the two minerals. Conversely a lesser amount of vanadium substitution should be revealed by an increase in intensity of the 002 reflection relative to the 001 and 003 reflections.

Figure 3 shows the X-ray patterns given by oriented aggregates for five Colorado Plateau samples in which mica is the principal constituent. All show a weak 002 reflection although in samples AW-207-54A and AW-146-52 this line is relatively stronger than in the other samples suggesting a lesser

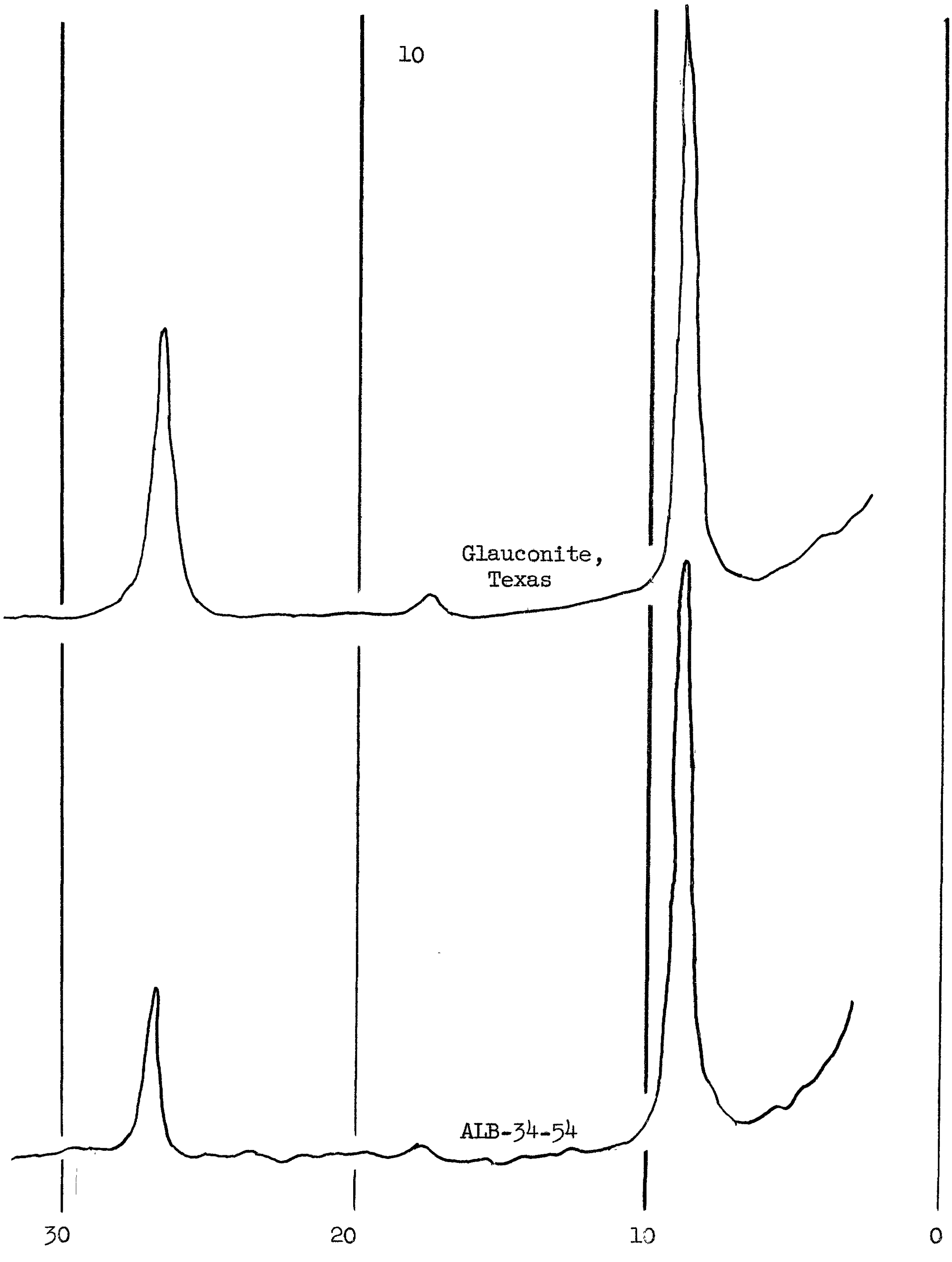

Figure 2.--Comparison of X-ray diffraction patterns of oriented aggregates of foscoelite and glauconite.

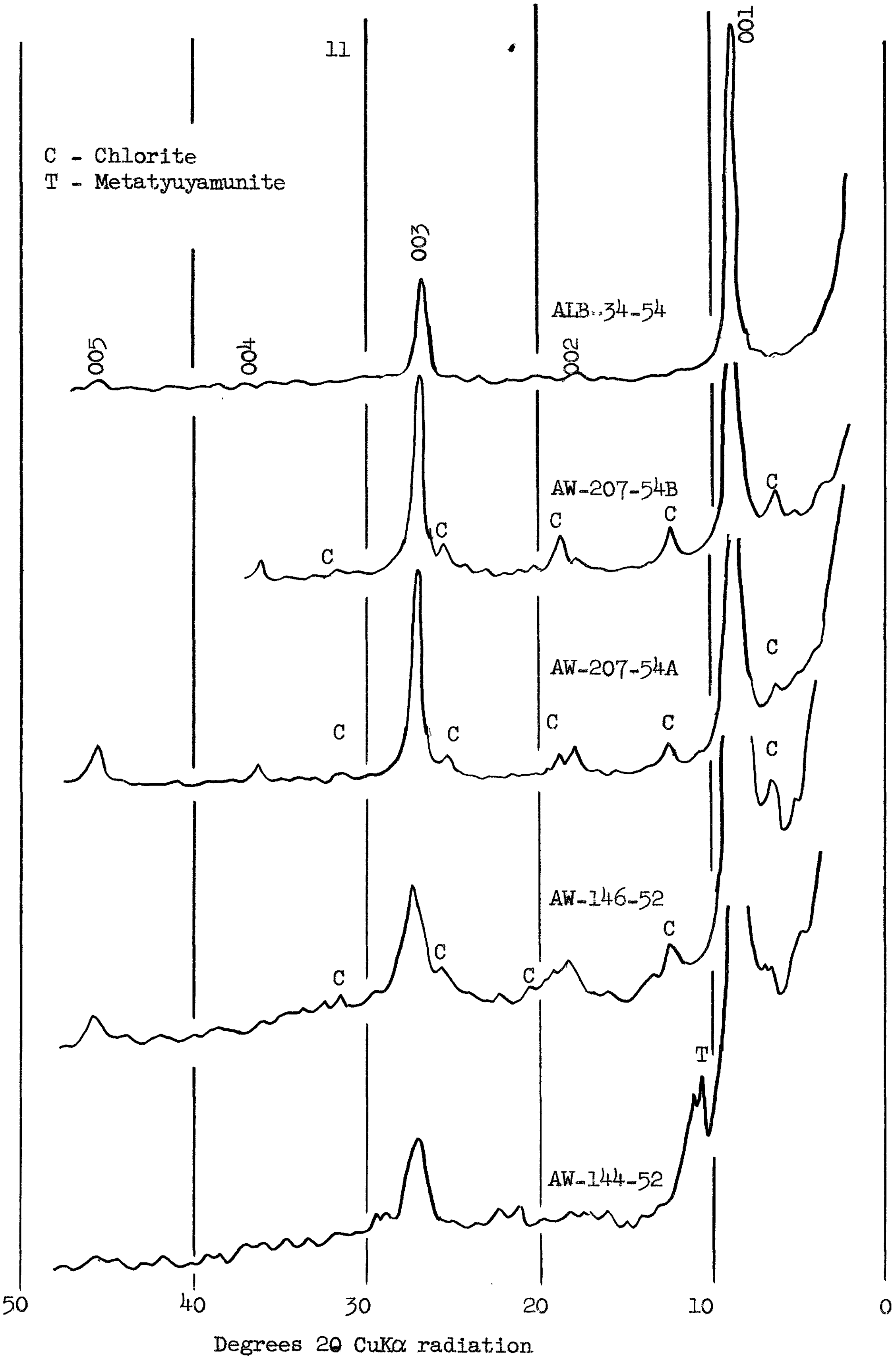

Figure 3.--X-ray diffraction patterns of oriented aggregates of five Colorado Plateau samples in which mica is the principal constituent.

amount of octahedral vanadium in these two samples. The patterns are arranged in order of decreasing degree of crystal perfection toward the bottom of the diagram, although the first three patterns show approximately equal crystallinity. Accompanying this decrease is an increase in the 001 spacing as tabulated below:

Sample no.	001 spacing in A
ALB-34-54	10.1
AW-207-54B	10.1
AW-207-54A	10.1
AW-146-52	10.3
AW-144-52	10.5

All of the samples in figure 3 except ALB-34-54 contain impurities as indicated on the diagram by "C" for chlorite and "T" for metatyuyamunite. Ethylene glycol treatment had little effect on samples ALB-34-54, AW-207-54B, and AW-207-54A, but some expansion took place in samples AW-146-52 and AW-144-52 as is shown in figure 4. The extreme loss in intensity suffered by the 001 reflection in these samples sometimes occurs through physical disruption of the surface of the oriented aggregate on glycol treatment. Such disruption did not occur with samples AW-146-52 and AW-144-52 therefore it is suggested that the loss of intensity is entirely the result of the expansion of montmorillonitic layers randomly interstratified with layers of roscoelite. These two samples might justifiably be called vanadium hydromicas in the sense that they are micaceous and contain vanadium and would show a high proportion of water in a chemical analysis; however, they might better be identified as mixed-layered mica-montmorillonite minerals which would acknowledge their expandable properties.

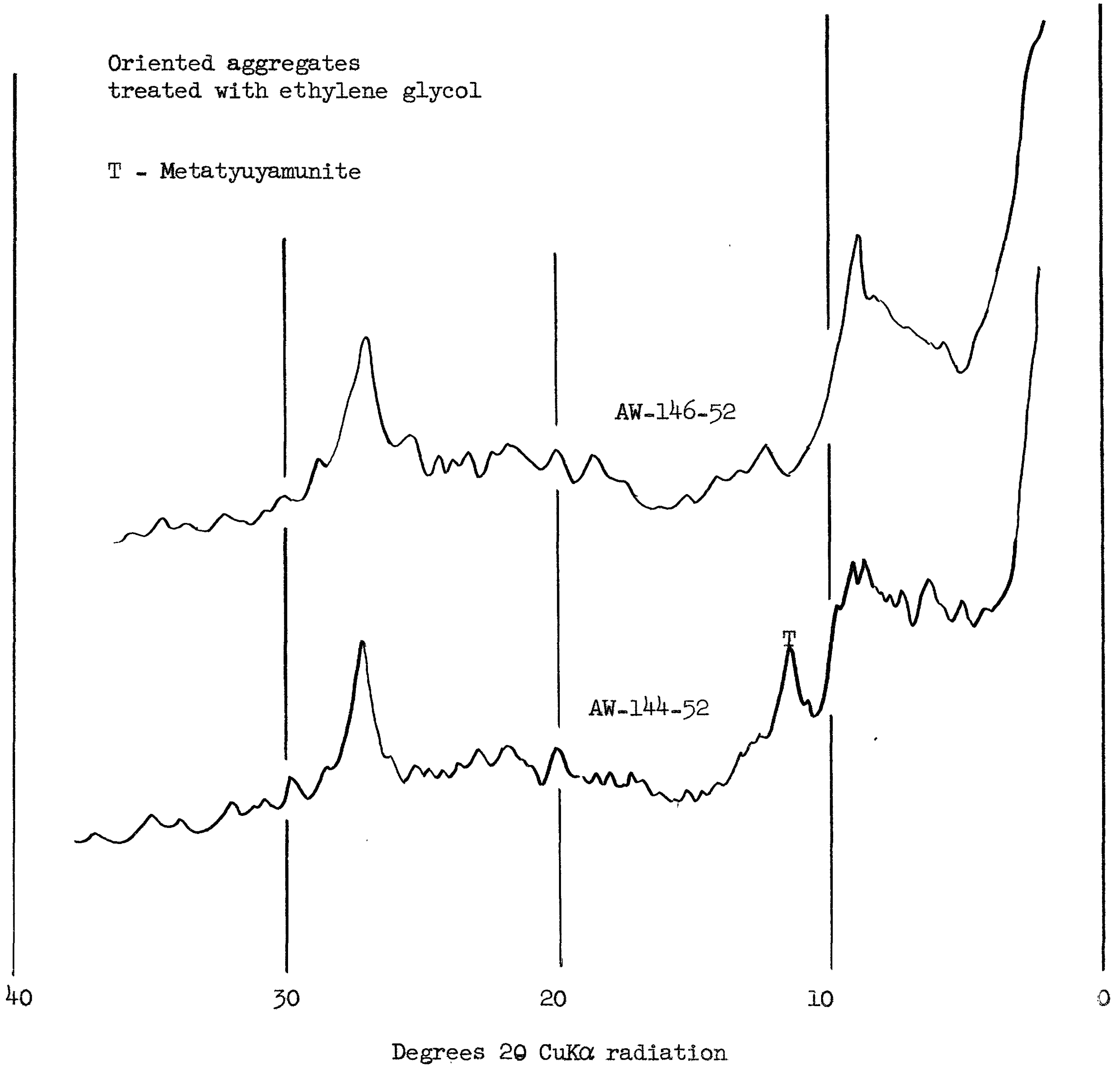

Figure 4.--X-ray diffraction patterns showing expansion of vanadium silicates treated with ethylene glycol.

A slightly different type of material is shown in figure 5 by sample AW-67-51. This sample is a mixture of at least two minerals, both of which expand slightly on ethylene glycol treatment. The shift of a peak at 12.9 A to 13.8 A is suggestive of a vermiculitic mineral, whereas the behavior of the other major component with a reflection at 10.6 A suggests a mixed-layered mineral similar to samples AW-144-52 and AW-146-52. Heat treatment however indicates that both of these minerals are less durable than either vermiculite or the mixed-layered minerals discussed above. At 400° C both AW-144-52 and AW-146-52 collapsed to structures closely resembling roscoelite and at 500° C still give lines of strong intensity. AW-67-51, on the other hand, gives evidence of destruction of the crystal lattice at 400° C, and at 500° C a new unidentified phase has appeared. Treatment of this sample with hot concentrated HCl leaves a residue which gives an X-ray pattern similar to that of roscoelite except that its structure is apparently destroyed between 400° and 500° C.

Sample G-53-53 (fig. 6) is an example of a mixture of chlorite and a mica which shows only a minor amount of interstratification with more highly hydrated layers as ethylene glycol and heat treatment affect the shape and position of the mica 001 reflection only slightly. The intensity of the 002 reflection after heat treatment at 500° C suggests that the mica is roscoelite with less substitution of vanadium for aluminum than in sample ALB-34-54. The chlorite in sample G-53-53 is characterized by the almost equal intensity of the first four 00ℓ reflections and by the accentuation of the first order reflection with loss of the higher orders after heat treatment at 500° C, a reaction that occurs in most well-crystallized chlorites. It should be noted that the chlorites in samples AW-207-54A and AW-146-52 behave similarly,

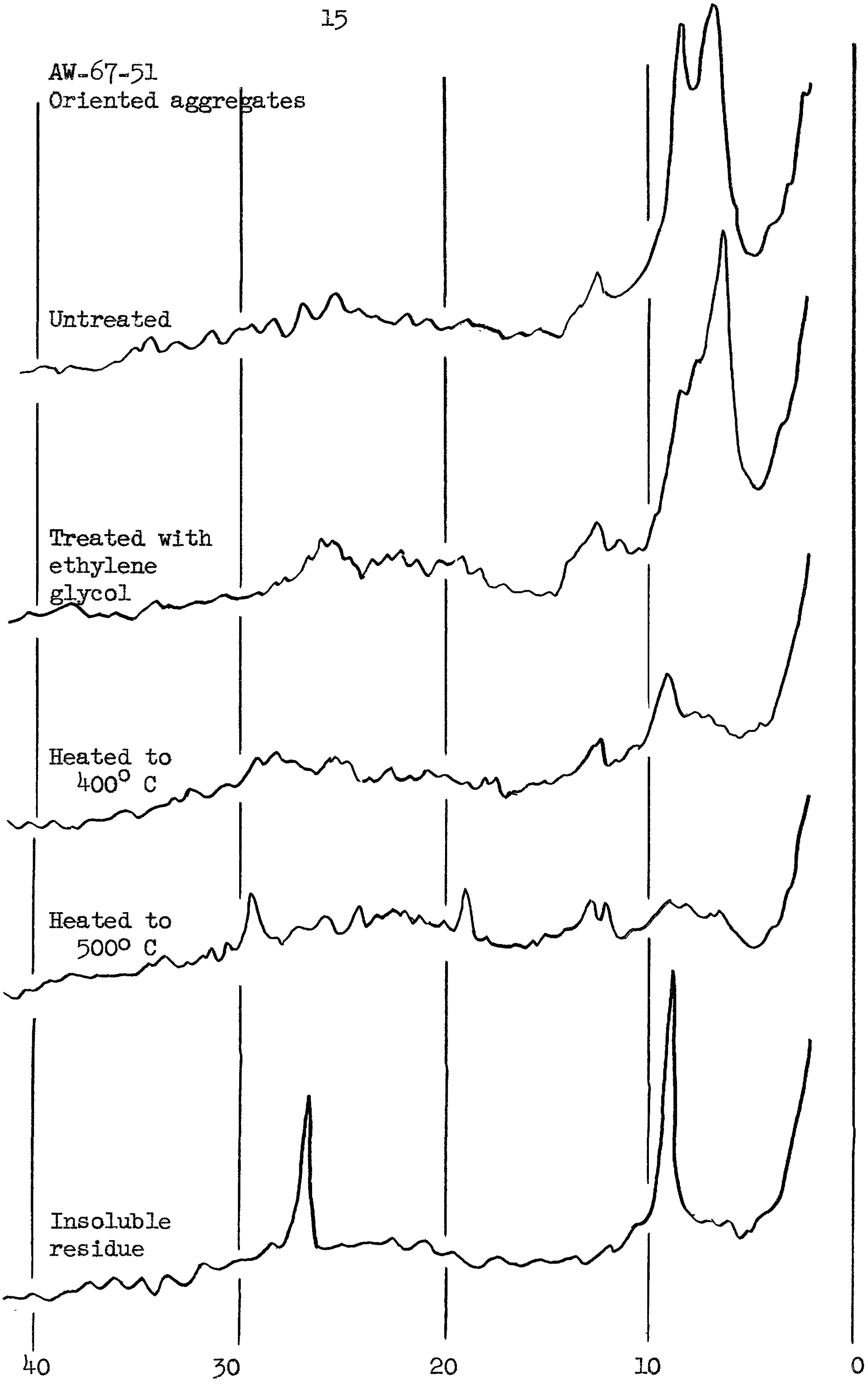

Figure 5.--X-ray diffraction patterns of AW-67-51 (a mixture of 2 or more minerals) showing shift in peaks caused by treating with ethylene glycol and by heating.

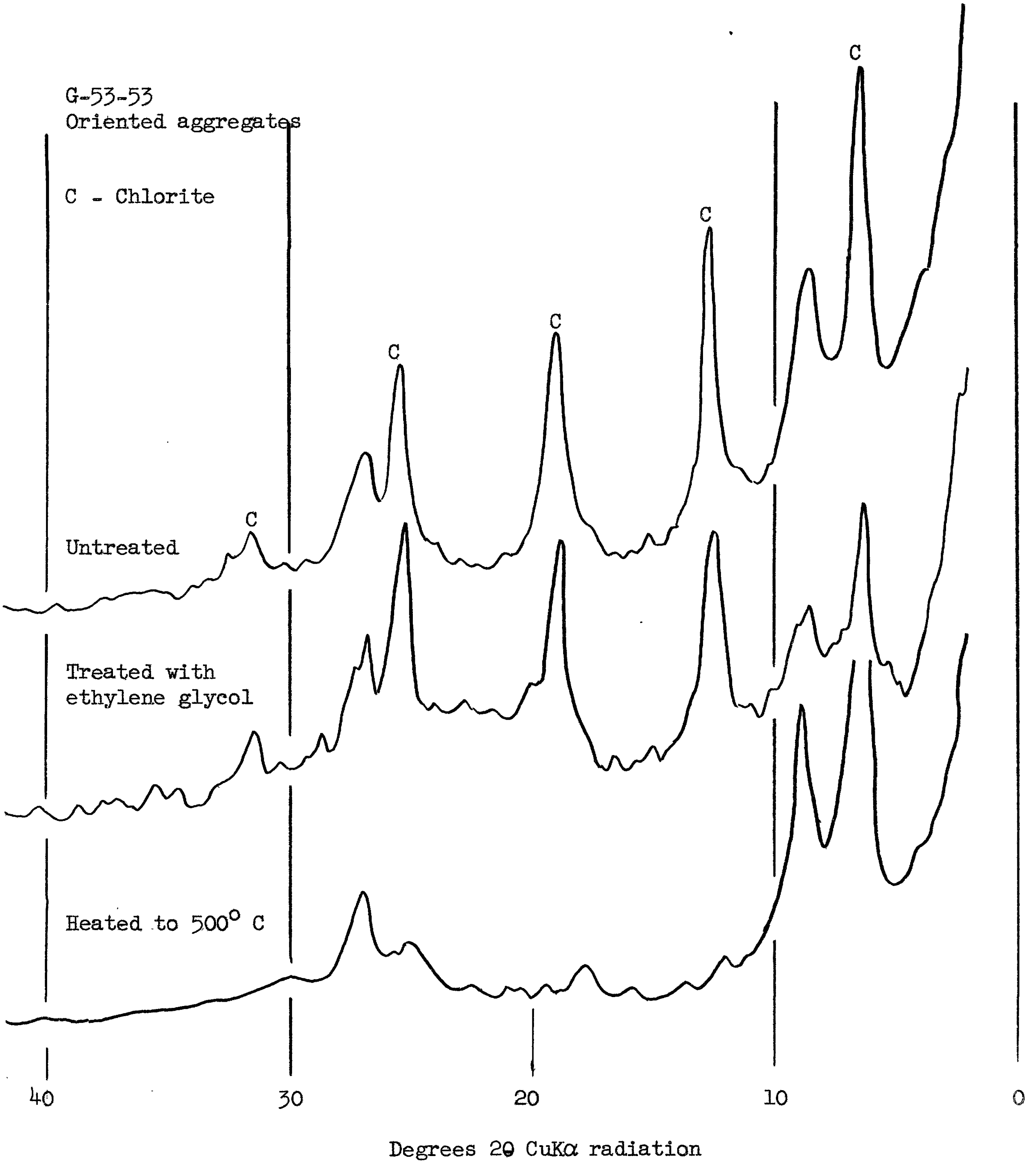

Figure 6.--X-ray diffraction patterns of sample G-53-53 untreated, after ethylene glycol treatment, and after heating.

whereas in AW-207-54B the increase in intensity of the 001 line fails to take place at elevated temperature, the chlorite lines disappearing and the lines of an unidentified new phase appearing at 400° C instead. At 500° C still another unidentified phase appears replacing the one occurring at 400° C. No experiments have been carried out as yet to determine if these phases are at equilibrium at the given temperatures. Inasmuch as sample AW-207-54B comes from unoxidized ore whereas AW-207-54A represents an oxidized zone, it seems possible that the oxidation state of the vanadium in the chlorite affects the stability of the mineral. The relationship, however, may be difficult to visualize when it is considered that the normal chlorite usually contains bivalent elements in both the octahedral layer and the interlayer brucite sheet. The manner in which vanadium III, IV, or V atoms are contained in a chlorite structure remains as a further problem of investigation.

Samples P-1-M-53 and P-1-P-53 from a channel sample taken at the Mineral Joe mine, Montrose County, Colo., were examined without purification other than size fractionation to concentrate the clay size particles. The X-ray patterns for oriented aggregates of the $<2\mu$ fraction of these samples are given in figure 7. Mica, chlorite, and carnotite are the principal constituents of the clay fraction of sample P-1-M-53. The mica and chlorite 001 reflections show slight shifts on treatment with ethylene glycol suggesting that they have montmorillonitic layers interstratified with them. Their behavior on heat treatment lends support to the supposition that the mica and chlorite are mixed-layered minerals, as a distinct shift toward lower spacings occurs after heating of the sample to 400° C. The characteristics of the first order chlorite reflection after heating is suggestive of a vermiculitic mineral except that the higher order 00ℓ reflections of the untreated material show intensities greater than those expected from a vermiculite.

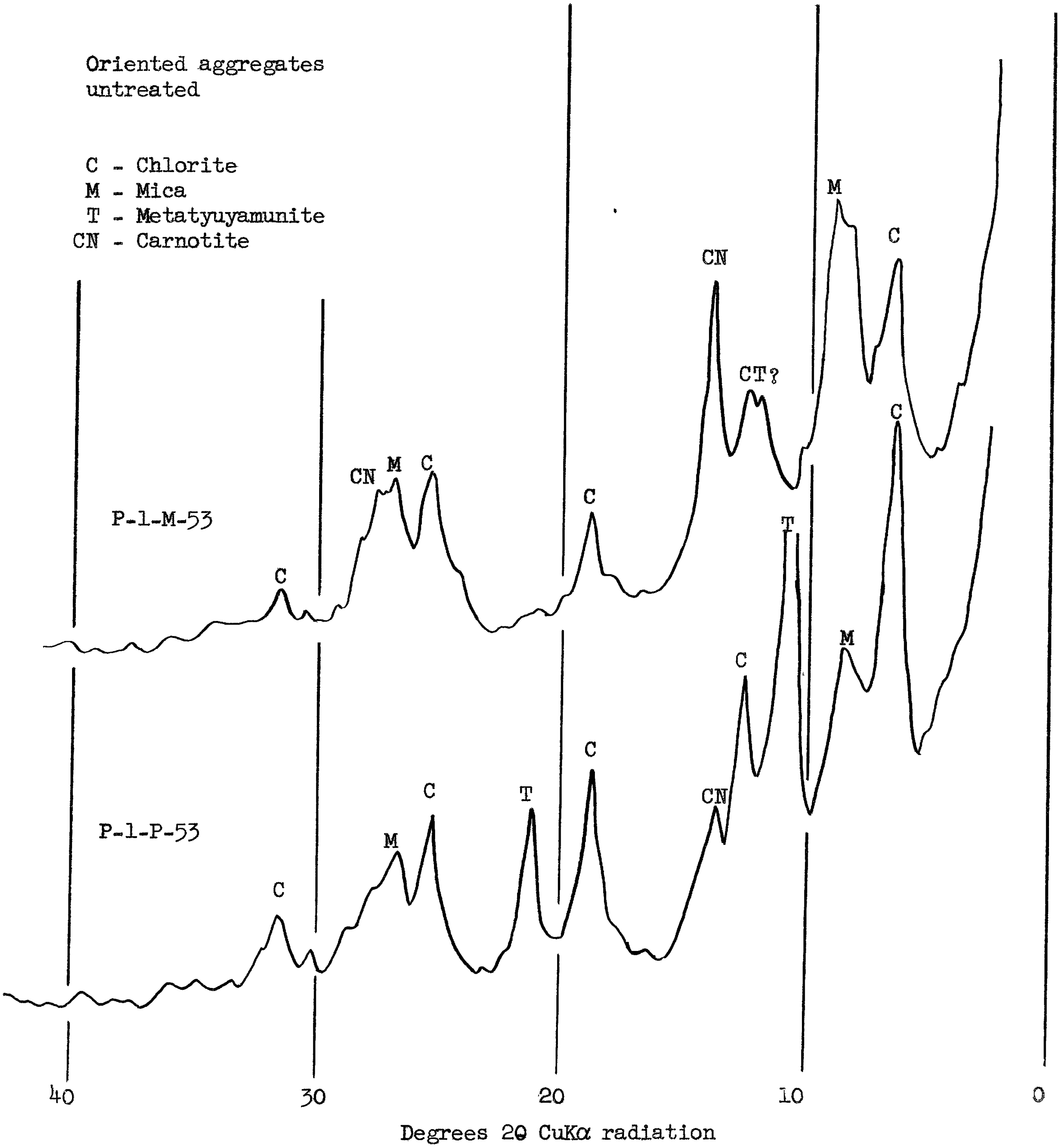

Figure 7.--X-ray diffraction patterns of oriented aggregates of two samples from the Mineral Joe mine, Montrose County, Colo.

Sample P-1-P-53 differs from the previous sample in that metatyuyamunite is present as a major constituent. Further differences are a higher degree of mixed layering in the mica and a chlorite which shows greater thermal stability closely resembling the chlorite of sample G-53-53. The mica in turn shows characteristics on ethylene glycol treatment similar to the mica of sample AW-144-52.

CONCLUSIONS

The vanadium silicates examined contain mica that varies from roscoelite (AMNH 13565) to highly mixed layered mica-montmorillonite (AW-144-52) in which the mica layers are probably roscoelite-like in octahedral composition but of very poor crystallinity. Chlorites are present in most of the samples and vary from types of high thermal stability and good crystallinity (G-53-53) to mixed-layered chlorite montmorillonite aggregates (P-1-M-53) and chlorites of poor thermal stability (AW-207-54B).

The samples might be grouped according to the character of each of their mineral components as follows:

Mica

Roscoelite → increasing mixed layering

AMNH 13565
ALB-34-54
AW-207-54A
AW-207-54B
G-53-53
P-1-M-53
AW-146-52
AW-67-51
P-1-P-53
AW-144-52

Roscoelite → decreasing octahedral substitution of V for Al (based on relative 002 intensity)

AMNH 13565
ALB-34-54
AW-207-54B
AW-144-52
AW-67-51
AW-207-54A
AW-146-52
G-53-53
P-1-M-53
P-1-P-53

Chlorite → increasing mixed layering

G-53-53
P-1-P-53
AW-207-54A
AW-207-54B
AW-146-52
P-1-M-53
AW-67-51 (vermiculite?)

Chlorite → decreasing thermal stability

G-53-53
P-1-P-53
AW-207-54A
AW-146-52A
P-1-M-53
AW-67-51 (vermiculite?)
AW-207-54B

The identification and analysis of the character of the constituents of the above samples were aided by the increased intensity of the diffracted lines and the simplification of the pattern afforded by the technique of using oriented aggregates of the fine fractions of the samples and by auxiliary treatment of these aggregates. In the writer's opinion single powder photographs or randomly oriented diffractometer mounts alone do not give sufficient data with which to characterize or to identify adequately many of the vanadium layer silicates studied.

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