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THE NATURE OF GARNIERITES—II ELECTRON-OPTICAL STUDY

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Abstract—Electron micrographs of 7 Å-type and 10 Å-type garnierites have been recorded at $5 \cdot 10^4$–10^5X magnifications to show the morphological character of these minerals, and at 10^6X magnification to show structural features of the particles. The 7 Å, serpentine-like minerals show a greater variety of morphological forms including tube- and rod-shaped particles and also platy forms and poorly defined, fluffy particles, probably aggregates. The 10 Å, talc-like minerals show mainly platy forms and fluffy aggregates, and generally very few tube or rod-shaped particles. At 10^6X magnifications, the 7 and 10 Å layer spacings are seen directly. In the samples examined, the 7 Å spacings are more clearly and more regularly defined than the 10 Å spacings.

INTRODUCTION

BECAUSE of their fine-grained and inhomogeneous character and their generally poor crystalline order, garnierites would seem to be very appropriate materials for electron-optical study. However, in a recent survey, Whittaker and Zussman (1971, p. 173) came to the conclusion that not all the difficulties related to garnierites had been resolved. Huggins (1961) reported briefly on a serpentine-like garnierite from Webster, North Carolina, which at 58,000X magnification showed bundles of extremely narrow ribbons, many less than 200 Å in cross-section. Kato (1961) studied garnierites from New Caledonia and gave electron micrographs, reproduced at about 9000X magnification, showing both fibrous and platy forms in samples which by X-ray diffraction appeared to resemble serpentine, talc, and chlorite minerals. Muchi (1965, 1966) described micrographs of 7- and 10 Å-type garnierites from Ōeyama mine, Kyoto prefecture, Japan, reproduced at about 25,000X magnification. The 7 Å-type, serpentine-like mineral showed very fine fibers of average width 230 Å, average length 1100 Å, and also rounded "cottony" forms probably consisting of aggregates of fine fibers. The 10 Å-type mineral also showed rounded particles which may consist of bundles of extremely fine fibers and also particles of amorphous or fluffy-appearing material. Faust *et al.* (1969) described a nickel analog of chrysotile, named pecoraite, which at $2 \cdot 10^5$X magnification showed particles of about 70 (±5) Å size in the form of curved plates and spirals.

The present study has been directed towards a clearer understanding of the 7 and 10 Å-type crystallizations found in most garnierites. From a preliminary survey of some 40 garnierites, samples were selected showing predominantly 7 Å, or predominantly 10 Å basal spacings, for detailed study by various methods. In the preceding paper (Brindley and Pham Thi Hang, 1972), hereinafter called "Part I", X-ray diffraction data, chemical and thermogravimetric analyses, and color characteristics are discussed. The electron-optical data, obtained by a collaborative investigation, are reported here.

EXPERIMENTAL

The selected samples were gently crushed and disaggregated by ultrasonic treatment in distilled water. Drops of suitably diluted suspensions were placed on thin, carbon-covered grids, and examined in a Phillips electron microscope, model EM300, with 100 kV electrons at magnifications in the range $5 \cdot 10^4$–10^5X. This part of the work was carried out by one of the authors, Pham Thi Hang, at The Pennsylvania State University. Care was taken to expose the particles for the minimum length of time to the electron beam. Long exposures caused bloating of the samples due to loss of water.

High resolution, high magnification micrographs of the same samples were obtained by one of the authors, N. Uyeda, at the University of Kyoto, Japan, using an Hitachi HU-12 electron microscope with 125 kV electrons. Magnifications up to 2×10^6X were obtained which gave direct images

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of the layer structures of these minerals, and enabled the 7 and 10 Å layer spacings to be readily distinguished. The electron optical magnification was calibrated with lattice images of reference crystals such as pyrophyllite and chlorinated Cu-phthalocyanine.

RESULTS

From the analytical data given in Part I, the following will be quoted for each of the samples discussed: Basal spacing, $d(001)$, in Å; the weight per cent NiO; and the estimated proportion x per cent of talc-like layers associated with serpentine-like layers in 7 Å-type garnierites, and of serpentine-like layers associated with talc-like layers in 10 Å-type garnierites, derived from the chemical analyses. Part I should be consulted for a discussion of the assumptions involved in deriving the values of x.

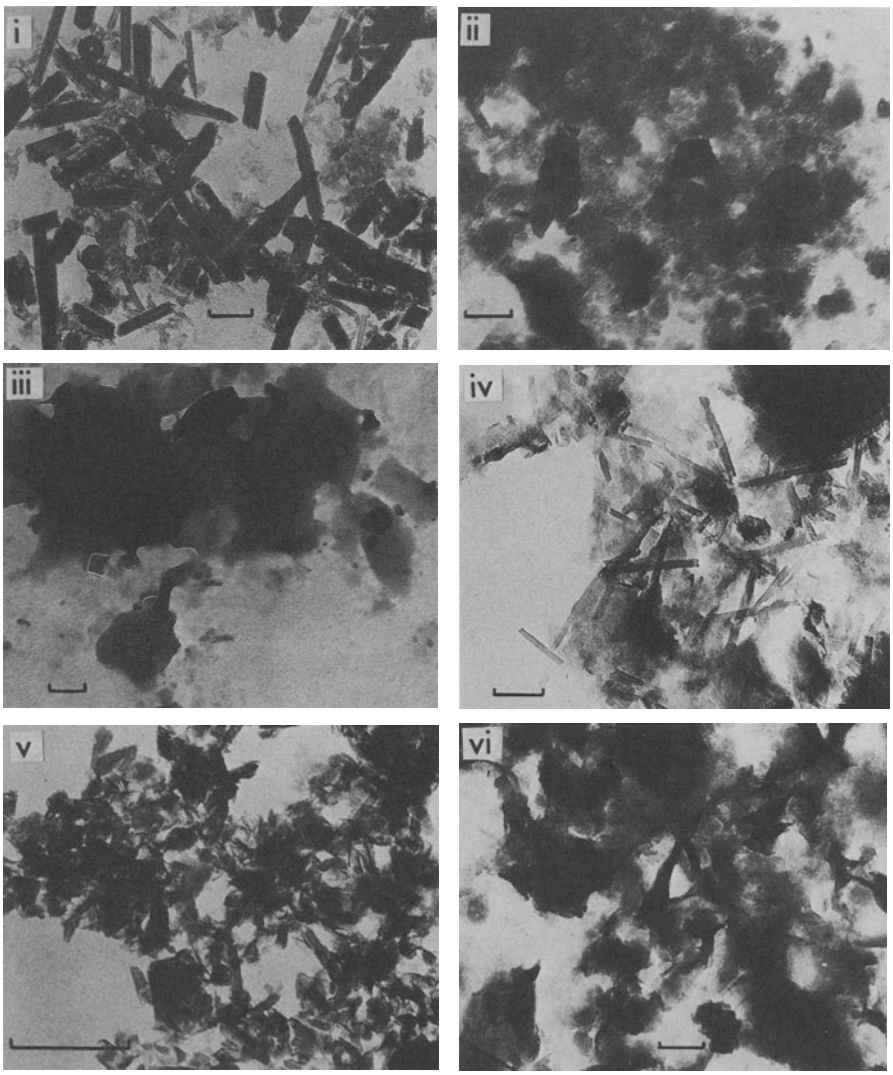


Fig. 1. Electron micrographs of predominantly 7 Å-type garnierites. Scale mark = 0·2μm. Samples illustrated: (i) MN6, Morro do Niquel, Brazil. (ii) 3996, Morro do Cerisco, Liberdade, Brazil. (iii) HMC5, Riddle, Oregon. (iv) Sample Serbia 2, from Village Ba. (v) Kambalda, Australia. (vi) New Caledonia.

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Fig. 2. Sample MN6 from Morro do Niquel, Brazil. Scale mark = 100 Å. White brackets indicate regions of clearly seen 7 Å spacings. Arrows point to wider spacings of about 10 Å interstratified with 7 Å spacings.

7 Å-type garnierites

Figure 1 shows at a glance the variety of morphological forms observed; there is a broad resemblance to the tubular and platy forms of the serpentine group minerals, chrysotile and lizardite. The scale mark on each micrograph is 0·2 μm.

Figure 1(i). Sample MN6 from Morro do Niquel, Brazil; 44300X magnification; $d(001) = 7{\cdot}28$ Å; 4·4 wt% NiO, $x = 13$ per cent.

Mainly short stubby tubes (or rods) are seen; average length is about 0·35 μ, average cross section about 0·08 μ. Three nearly circular sections are seen with thin central holes. Particles seen length-wise appear to be thick-walled. Some thinner tubes and a few ill-defined platy fragments are seen.

At 10^6X magnification in Fig. 2, flattened tubes or rolled forms are seen with well-defined 7 Å spacings on the flat sides, but only vestiges of layers are seen where the curvature is high; white brackets indicate where these spacings are most clearly seen. Also seen are 7 Å spacings running parallel to the particle length and visible over a large part of the particle width. Scattered among the 7 Å spacings are a few regions where wider spacings of about 10 Å can be seen, some of which are indicated by arrows. At the center of the elongated particle where the 7 Å spacings are no longer visible, moiré fringes are observed apparently produced by the tubular structure. The widths of various particles measured at 10^6X magnification are 700, 850, 850, 600, 800 and 650 Å, with an average of 740 Å, in agreement with the lower magnification measurements.

Figure 1 (ii). Sample 3996 from Morro do Cerisco, Liberdade, Brazil; 51,000X magnification; $d(001) = 7{\cdot}27$ Å; 5·5 wt% NiO; $x = 20$ per cent. The particles have mainly poor outlines and rather platy character. Very few tubular or rod-shaped particles are observed. High magnification micrographs were not taken. X-ray diffraction indicates a disordered lizardite-like material.

Figure 1 (iii). Sample HMC5, from Riddle, Oregon; magnification 33,000X; $d(001) = 7{\cdot}31$ Å; 18·6 wt% NiO; $x = 27$ per cent. The particles have mainly a poorly defined, fluffy appearance, and very few tubes are seen. This sample contains the highest estimated proportion of talc-like layers, 27 per cent. At 10^6X magnification, Fig. 3, it is difficult to find a clear succession of 7 Å spacings, and many regions are found where 2 or 3 layers exhibit a 10 Å spacing, presumably the talc-like

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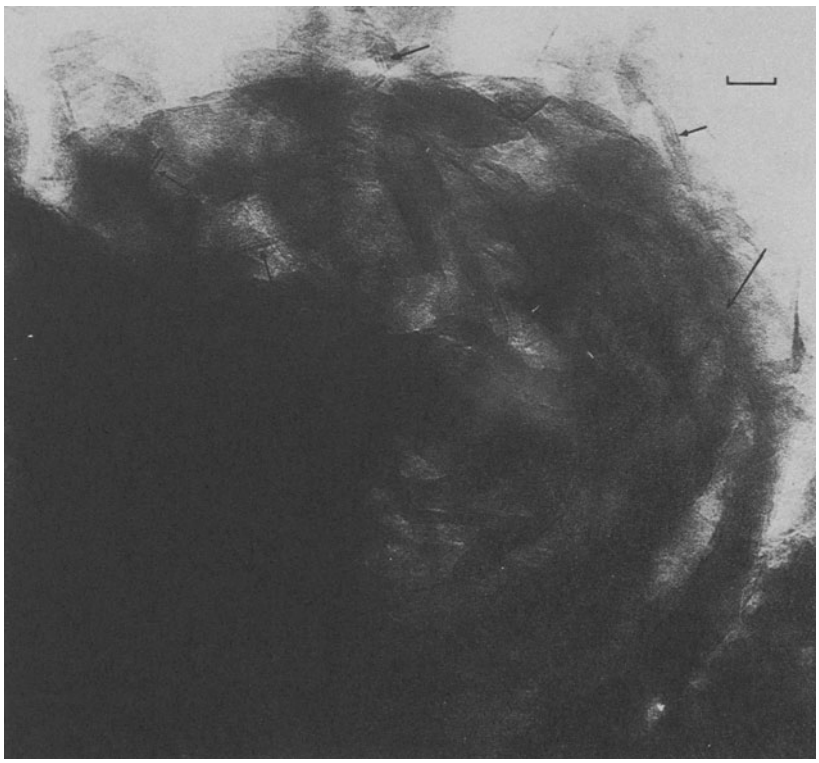


Fig. 3. Sample HMC5, Riddle Oregon. Arrows point to spacings of about 10 Å. Scale mark = 100 Å.

component, a result which is consistent with the high value of X, 27 per cent, for this material. The most interesting feature shown in Fig. 3 is the resemblance to a curved, or incipient tube-like, arrangement.

Figure 1 *(iv)*. Sample Serbia 2, from Village Ba, Serbia, $d(001) = 7{\cdot}34$ Å; the sample was insufficiently pure for chemical analysis; estimated NiO, 27 per cent. At 55,000X magnification, a mixture of thin tubular particles, ill-defined platy and agglomerated particles are seen. No high magnification micrographs were taken.

Figure 1 *(v)*. Sample from Kambalda, Australia, $d(001) = 7{\cdot}28$ Å; the sample was insufficiently pure for chemical analysis; estimated NiO, 43 per cent. At 132,000X magnification, short rod-like (tubular) particles are seen, many about $0{\cdot}1\ \mu$ long and $0{\cdot}02\ \mu$ cross-section. No high magnification micrographs were taken.

Figure 1 *(vi)*. Sample from New Caledonia, $d(001) \simeq 7{\cdot}7$ Å; (001) X-ray peak profile spreads towards smaller 2θ values, indicating the presence of longer spacing material, 49·3 wt% NiO, X = 19%. This sample contains the highest observed NiO content among the 7 Å-type minerals studied, and is only slightly less than that of pecoraite, 51·5 per cent NiO, studied by Faust *et al.* (1969). At 51,000X magnification, the mineral is seen to consist of rolled, flaky material, resembling micrographs of montmorillonite; many of the twisted flakes appear to be very thin. The mineral when placed in water, does not show the swelling behavior of montmorillonite, but when placed in ethylene glycol a part of the mineral shows some swelling.

At 10^6X magnification, layer spacings of about 7 Å are observed in various forms; Figure 4 reproduces portions of several micrographs. In Fig. 4(a), edges of apparently twisted material show many twisted 7 Å spacings. Of considerable interest are the clearly defined layers at the ends or edges of flaky material where, for example, 13 spacings in a distance of 100 Å are easily counted, (Fig. 4b), and give a value of $d(001) = 7{\cdot}7$ Å in agreement with the X-ray data. Flattened tubes and rolled forms are seen in Fig. 4(c) with 7 Å spaced layers parallel to the flattened sides. As many as 15 consecutive layers can be counted cor-

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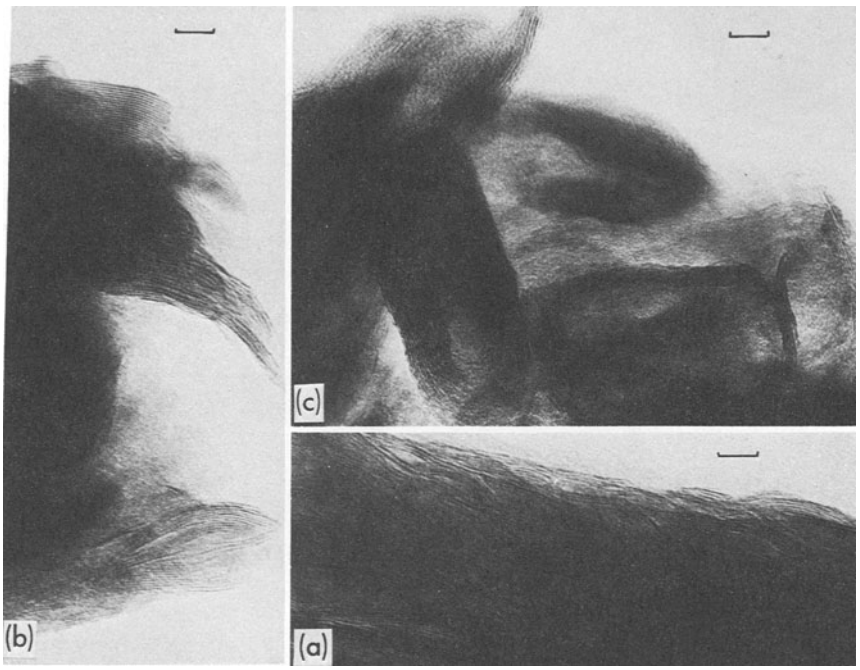


Fig. 4. Sample from New Caledonia. Observe the clearly defined 7 Å spacings in (a), the twisted spacings in (b), the rolled forms in (c). Scale marks = 100 Å.

responding to a wall thickness of about 100 Å. The particle thickness is about 300 Å. The material forming the core of the flattened tube appears to be highly disordered, but it is difficult to know if the material is amorphous.

10 Å-type garnierites

Micrographs at $5 \cdot 10^4$–10^5X magnification are shown in Fig. 5 which indicate that the 10 Å-type garnierites exhibit less morphological variety than the 7 Å-type. The scale mark on each micrograph is 0·2 μm. Except in Fig. 5(iii), elongated particles, tubes, laths, rods, are rare or absent. The morphology generally can be described as poorly defined, platy or fluffy aggregates. At 10^6X magnifications, some interesting features are obtained which are considered below.

Figure 5 (i) and Figure 6. A so-called β-kerolite from Mount Goles, Yugoslavia. $d(001) = 10 \cdot 5$ Å, asymmetric profile; 0·26 wt% NiO; $x = 15 \cdot 5\%$. This is a nearly pure magnesian mineral.

This sample, presented by Dr. Z. Maksimovic, has been described by him as consisting of "irregular fluffy masses with ill-defined edges and very small particles", and having a 10 Å layered, non-expanding, talc-like structure (Maksimovic, 1966).

The exceptionally thin layers are clearly seen at 10^6X magnification in Fig. 6. The basal spacings are not directly visible; the planar surfaces are probably the basal planes.

Figure 7. Sample from Durham, North Carolina. $d(001) = 9 \cdot 94$ Å, asymmetric profile. 5·51 wt% NiO; $x \simeq 0$. Micrographs taken of 55,000X magnification are very similar to Figs 5(i) and (ii) and are not reproduced here. At 10^6X magnification, twisted masses showing 10 Å spacings are observed; in Fig. 7, most of the material shows 10 Å spacings, but some areas with 7 Å spacings can be found. It is very noticeable that rather few consecutive 10 Å spacings are found, whereas the 7 Å spacings give better layer sequences.*

Figure 5 (ii), (iii), (iv), (v), (vi). These micrographs correspond to the following samples:

Figure 5 (ii) Sample RO3B, Riddle, Oregon, 18·2 wt% NiO, $x = 15$ per cent, (iii) Sample RO24, Riddle, Oregon, 19·6 wt% NiO, $x = 36$ per cent,

*There is, of course, some inconsistency between $x \simeq 0$ derived in Part I from the chemical analysis, and the existence of 7 Å spacings in the micrographs. The evaluation of x rests on the validity of assuming ideal occupancy of tetrahedral and octahedral cation sites. It was not practicable to take large numbers of high magnification micrographs to obtain a statistical estimate of the proportion of 7 Å layers.

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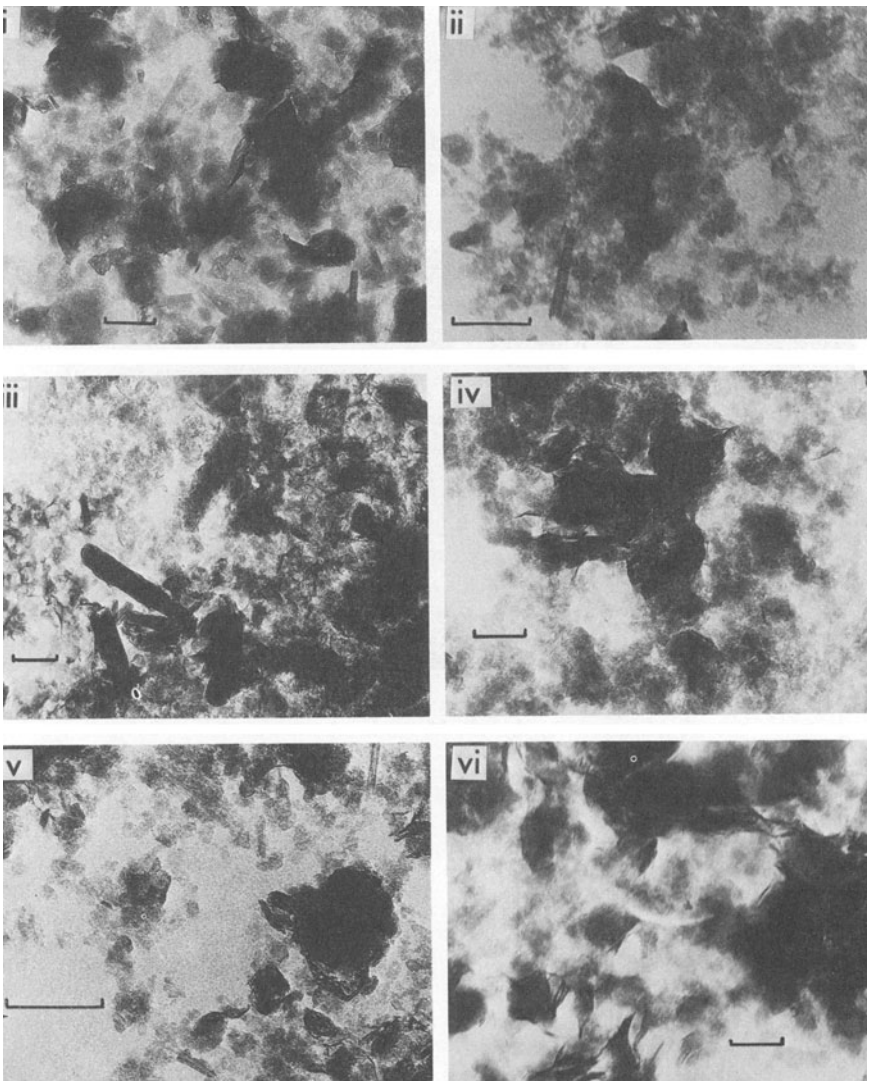


Fig. 5. Electron micrographs of predominantly 10 Å-type garnierites. Scale mark = 0·2 μm. Samples illustrated: (i) β-kerolite, Goles Mountain, Yugoslavia. (ii) RO3B, Riddle, Oregon. (iii) RO24, Riddle, Oregon. (iv) RO3A, Riddle Oregon. (v) Sample GUS, of unknown origin. (vi) Sample 201, Village Ba, Serbia.

(iv) Sample RO3A, Riddle, Oregon, 20·8 wt% NiO, $x = 9$ per cent, (v) Sample GUS, unknown source, 31·5 wt% NiO, $x = 27$ per cent, (vi) Sample 201, Village Ba, Yugoslavia, not analyzed.

These samples give $d(001)$ in the range 10·2–10·5 Å, all with asymmetric (001) X-ray peak profiles. Only 5(iii) shows prominent tube- or rod-like forms similar to those of Fig. 1(i).

Micrographs at 10^6X magnification of the material illustrated in Fig. 5(iii) show mainly tangled masses of 10 Å layered material, rarely exhibiting more than three or four parallel layers as in Fig. 8.

Figure 9. Shows a micrograph recorded at 1·5–10^6X magnification of the sample illustrated in Fig. 5(v), from an unknown source but probably from New Caledonia. This material is dominantly of 10 Å-type, but Fig. 9 also shows regions of 7 Å spacing. Also of special interest is the very clear indication of a 4·5 Å spacing along the layers. This

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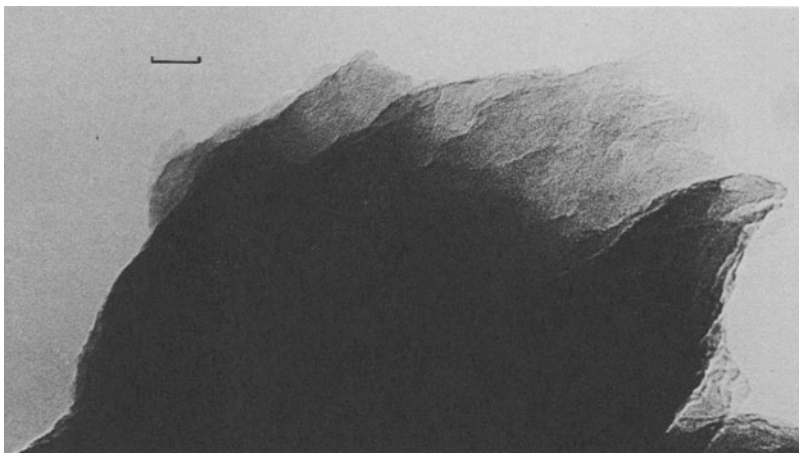


Fig. 6. β-kerolite, Goles Mountain, Yugoslavia. Scale mark, 100 Å. Observe the extremely thin plates, probably single layers.

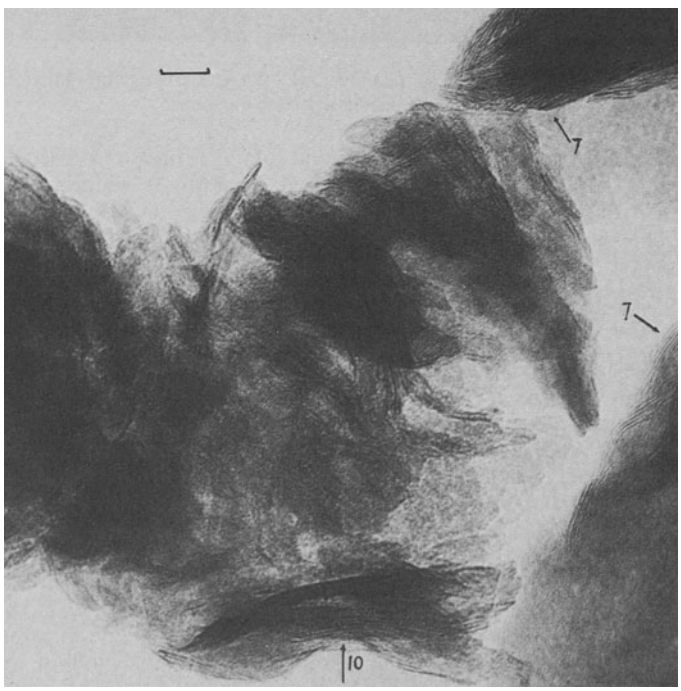


Fig. 7. Sample from Durham, North Carolina. Scale mark, 100 Å. Arrows point to regions where 7 Å and 10 Å layer spacings are most clearly seen.

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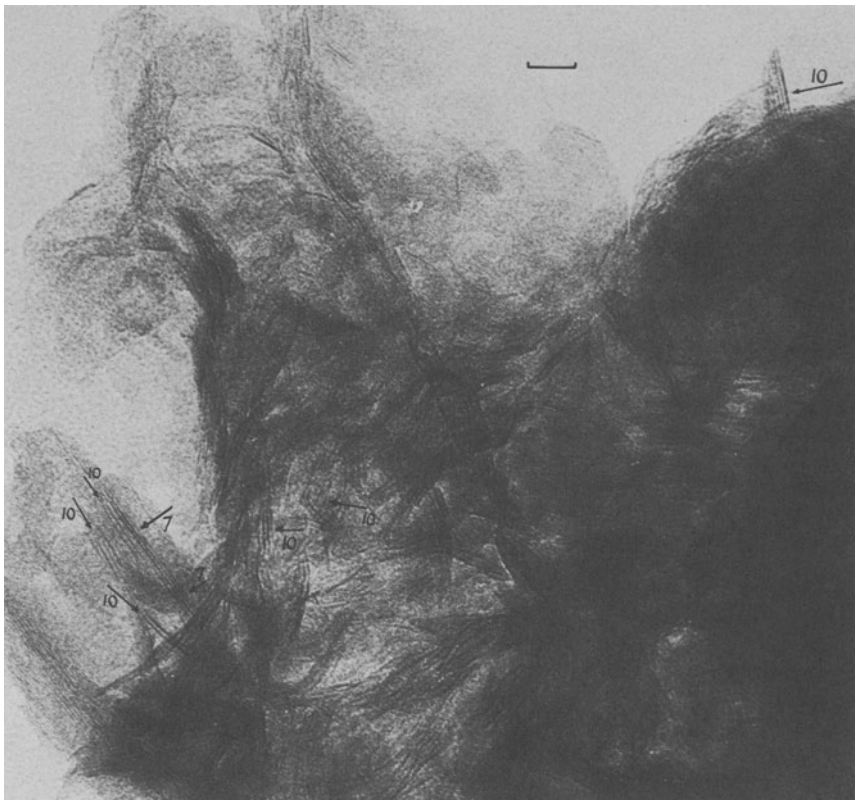


Fig. 8. Sample RO24, Riddle, Oregon. Scale mark 100 Å. Arrows point to regions where 7 Å- and 10 Å-spacings are seen most easily.

spacing corresponds to $d(020)$, i.e. b/2. High magnification micrographs of other samples also have revealed this spacing. In this micrograph, is seen the close association of 7 and 10 Å layers within what is apparently a single particle, and in some regions there appears to be an alternation (interstratification) of 7 and 10 Å spacings.

DISCUSSION AND CONCLUSIONS

Among the 7 Å minerals a greater variety of forms exists than among the 10 Å minerals. This result is broadly consistent with the variety of serpentine minerals (chrysotiles, lizardite, antigorite...) and the generally similar forms of talc-like minerals. Antigorite in the strict sense of a serpentine mineral with a long a parameter has not been found in the garnierites studied.

There does not appear to be a close correlation between the proportions of elongated and platy particles observed at 10^4–10^5X magnification, and the proportions of serpentine-like and talc-like layers estimated from the chemical compositions, i.e. the values of x. A partial explanation may be that platy forms can arise from both kinds of crystallization. A second consideration is that 7 and 10 Å-type layers may be intermixed within a single particle, in the form of interstratifications or as partial segregations; Fig. 9 illustrates these possibilities.

It is very noticeable at 10^6X magnification that the 7 Å spacings are always more clearly and more regularly defined than the 10 Å spacings. Many examples have been found where as many as ten to twenty of the 7 Å spacings have been observed in a measurable sequence, whereas the 10 Å spacings are revealed by no more than about three or four parallel layers. A possible explanation may relate to the hydration of the talc-like layers, discussed in Part I of this study.

No correlation has been observed between the weight per cent of NiO in the analyzed samples and their morphology. In other words, Ni^{2+} ions replace Mg^{2+} ions without a major effect on the crystal morphology of these minerals, which therefore must be governed by other considerations.

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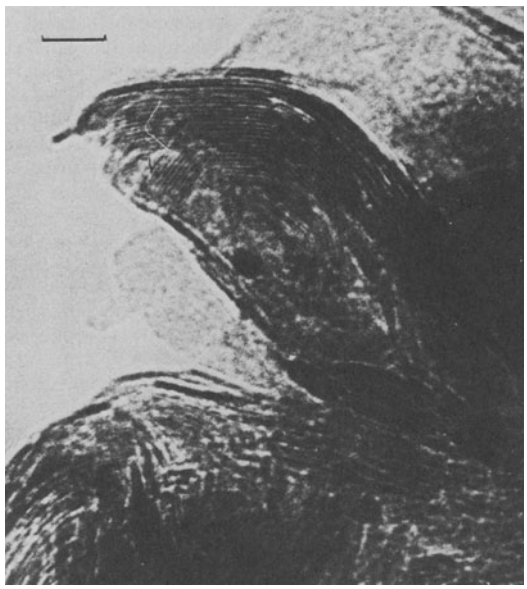


Fig. 9. Sample GUS, garnierite from unknown source. Scale mark 100 A. Observe the very clear 7 Å spacings in the upper part of this figure, with 4·5 Å spacing along the layers.

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Résumé—Les micrographies électroniques de garniérites du type 7 Å et 10 Å ont été effectuées à des grandissements de $5 \cdot 10^4$ à 10^5 fois afin d'établir la morphologie de ces minéraux et à un grandissement de 10^6 fois afin d'étudier les caractéristiques structurales des particules. Les minéraux à 7 Å du type serpentine montrent la plus grande variété morphologique avec des particules en tubes et en bâtonnets, des formes plates mal définies, et des particules floconneuses, probablement des agrégats. Les minéraux à 10 Å du type talc montrent surtout des formes plates et des agrégats floconneux, et en général très peu de particules en tubes ou en bâtonnets. Au grandissement 10^6 fois, on voit directement les espacements à 7 Å sont définis d'une façon plus claire et plus régulière que les espacements à 10 Å.

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Kurzreferat – Elektronenmikrogramme von 7 und 10 Å Garnieriten wurden mit $5 . 10^4 - 10^5$ X Vergrößerungen aufgenommen, um die morphologische Beschaffenheit dieser Mineralien zu erweisen, sowie mit 10^6 X Vergrößerung, um die strukturellen Eigenschaften der Teilchen aufzuzeigen. Die 7 Å serpentinartigen Mineralien weisen eine größere Vielfalt morphologischer Formen auf, einschließlich rohrund stabförmiger Teilchen, scheibenartiger Formen und unklar abgegrenzter flockiger Teilchen, die wahrscheinlich Aggregate sind. Die 10 Å talkartigen Mineralien sind hauptsächlich scheibenförmig und enthalten flockige Aggregate, aber im allgemeinen sehr wenige rohr- oder stabförmige Teilchen. Bei 10^6 X Vergrößerung sind die 7 und 10 Å Schichtungen sofort ersichtlich. In den untersuchten Proben waren die 7 Å Strukturen klarer und regelmäßiger als die 10 Å Strukturen.

Резюме — Электронные микроснимки гарниеритов типа 7 Å и 10 Å увеличили в $5{,}10^4$–10^5 раз для выявления морфологического характера этих минералов, а для обнаружения структурной особенности зерен применялись увеличения в 10^6 раз. Серпентинообразные минералы 7 Å имеют большое разнообразие морфологических форм, включая трубчатые и шестоватые частицы и также плетенные и незаметно пушистые частицы, наверно, сростки пород. Талькообразные минералы 10 Å имеют пушистую форму и редко трубчатые или шестоватые частицы. При увеличении в 10^6 раз непосредственно видно расположение слоев 7 Å и 10 Å. В рассматриваемых образцах нашли, что расположение слоев 7 Å более ясно выражено и резко очерчено, чем расположение слоев 10 Å.

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