*Clays and Clay Minerals*, 1973, Vol. 21, pp. 51–57. Pergamon Press. Printed in Great Britain

# THE NATURE OF GARNIERITES—III THERMAL TRANSFORMATIONS

PHAM THI HANG and G. W. BRINDLEY
Department of Geosciences, and Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.

(*Received* 25 *August* 1972)

**Abstract**—Serpentine- and talc-like garnierites described in Parts I and II were heated at various temperatures up to about 1000°C and after each treatment were cooled and examined by X-ray powder diffraction. The serpentine-like garnierites at about 550°C, the temperature at which rapid dehydroxylation begins, formed a highly disordered phase. When the NiO content was low (approximately < 20 wt%), the disordered phase transformed directly to an olivine phase around 800°C, but when the NiO content was higher, various transitional phases were formed before an olivine phase appeared around 1000°C. A sepiolite-like phase was obtained with one sample around 800°C, and several samples showed face-centered cubic modifications between 900 and 1000°C.

The talc-like garnierites with low NiO content formed an enstatite phase around 800°C directly following the dehydroxylation reaction, but with high NiO contents an olivine phase became increasingly prominent between 850 and 1000°C. Identification of the mixed crystallizations possibly existing in the initial minerals is scarcely feasible on the basis of the products formed up to 1000°C.

## INTRODUCTION

THE THERMAL transformations of garnierite are of interest in themselves and for their potential usefulness as a further method for studying the nature of the initial minerals, as emphasized by Vitovskaya and Berkhin (1968, 1970). It has been shown in Parts I and II* that many garnierites appear to be defective structures, and possibly exist as intimate mixtures of serpentine- and talc-like components. If these components transform at appropriate temperatures independently and in characteristic ways, then the results may shed light on the nature of the initial minerals.

The phase relations in the $MgO$–$NiO$–$SiO_2$ system have been been studied at 1400°C by Campbell and Roeder (1968) and their diagram on a mole percentage basis is given later, (see Fig. 6). The results of the present study can be compared only approximately with those of Campbell and Roeder because of the presence of other oxides, particularly $Al_2O_3$ and $Fe_2O_3$, in the natural materials and also because of the lower temperatures used. The ternary diagram shows that Ni replaces Mg in the enstatite phase only to a small extent, corresponding at the most to about 7 mole percent NiO, but replaces Mg in all proportions in the olivine phase.

At temperatures sufficiently high for equilibrium to be established, serpertine and talc minerals transforms as follows:

$$\underset{\text{serpentine}}{Mg_3Si_2O_5(OH_4)} \rightarrow \underset{\text{olivine}}{Mg_2SiO_4} + \underset{\text{enstatite}}{MgSiO_3} + 2H_2O. \quad (1)$$

$$\underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} \rightarrow \underset{\text{enstatite}}{3MgSiO_3} + SiO_2 + H_2O. \quad (2)$$

Up to about 900°C, however, serpentine forms mainly olivine in considerably greater amount than according to (1), and follows almost quantitatively the reaction, (Brindley and Hayami, 1964, 1965):

$$Mg_3Si_2O_5(OH)_4 \rightarrow (3/2)\,Mg_2SiO_4 + (1/2)\,SiO_2 + 2H_2O. \quad (3)$$

The expected reactions for Ni-containing minerals can be summarized in the following tabulation:

| | 7Å-type, serpentine-like garnierite | 10Å-type, talc-like garnierite |
|---|---|---|
| Low NiO content | Mainly olivine phase (equation 3), but possibly some enstatite (equation 2) | Enstatite phase (equation 2) |
| High NiO content | Olivine phase (equation 3 and phase diagram) | Olivine phase (phase diagram) |

*Part I, by G. W. Brindley and Pham Thi Hang, discusses X-ray diffraction data, chemical analyses, thermogravimetric data, and color characteristics; Part II by N. Uyeda, Pham Thi Hang and G. W. Brindley discusses electron optical data. These will be referred to respectively as Part I and Part II.



https://doi.org/10.1346/CCMN.1973.0210108 Published online by Cambridge University Press

If the initial minerals are mixtures, the phase development will depend also on the distribution of nickel between the components, provided they transform individually.

The experimental results will be considered in relation to this tabulation.

## EXPERIMENTAL RESULTS

Garnierite samples already described in Parts I and II were heated in air in small platinum crucibles for periods of about 3 hr successively at the following temperatures: 110, 250, 550, 600, 800, 850, 900, 950 and 1000°C, and after each heating were cooled in air and examined by X-ray diffraction, (filtered CuK$\alpha$ radiation, 1°(2$\theta$)/min recording rate, 2–64° 2$\theta$).

The results are summarized in Tables 1 and 2, and illustrated in Figs. 1–5. Figure 6 reporduces the equilibrium diagram obtained at 1400°C by Campbell and Roeder (1968), redrawn on a mole per cent basis, and sample compositions are plotted from the data in Part I, Tables 1 and 2, with (Mg + 3/2 $R^{3+}$)O used in place of MgO. For the most part it makes little difference whether the small proportions of $R^{3+}$ ions are taken into account or ignored.

## DISCUSSION

### *Serpentine-like, 7Å-type garnierites*

The results, summarized in Table 1 and illustrated in Figs. 1, 2 and 3, show the following main characteristics: A disordered phase exists

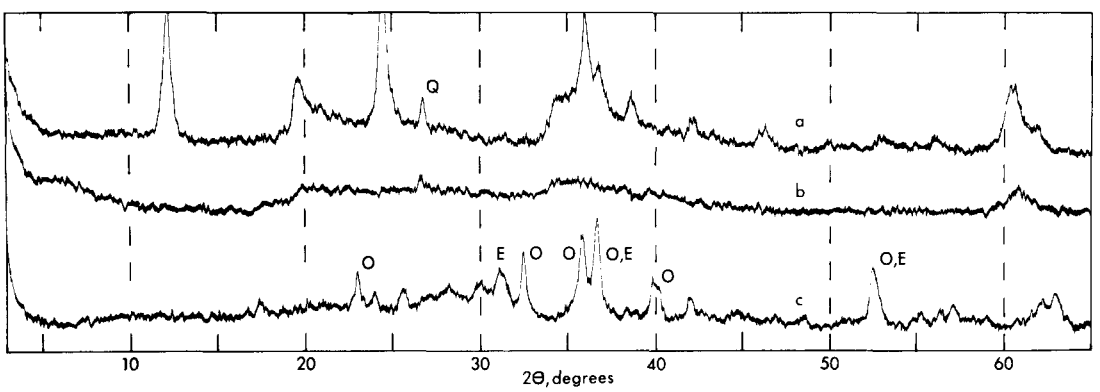



Fig. 1. Diffractometer patterns for sample MN6, 4·4 wt % NiO, after heating at (a) 110°C, (b) 600°C, (c) 800°C; CuK$\alpha$ radiation. Q = quartz, O = olivine, E = enstatite.

Table 1. Summary of thermal transformations of 7 Å-type garnierites

| Sample | Wt % NiO | Composition point in Fig. 6 | Temp. (°C) | X-ray diffraction data | Diffraction patterns |
|---|---|---|---|---|---|
| MN6 | 4·4 | 1, * | 600 | Disordered phase formed; hk diffraction bands, | |
| HMC5 | 18·6 | 3, * | | Broad peak ~ 6°(2$\theta$), 14–15 Å. | Fig. 1 |
| Analytical data, | | | 800 | Mainly olivine phase, minor enstatite | |
| Part I, Table 1 | | | 1025 | Mainly olivine, minor enstatite | |
| Serbia 2 | ~ 27 | | 500 | Disordered phase formed<br>Broad peak ~ 6°(2$\theta$), 14–15 Å | |
| | | Estimated NiO, Part I, Table 3 | 800 | Sepiolite-like phase formed<br>Prominent peak ~ 7·5°(2$\theta$), 12 Å | Fig. 2 |
| | | | 1000 | Face-centered cubic pattern<br>Longer heating gives slow development of olivine phase | |
| Kambalda | ~ 42 | | 550 | Disordered phase formed | |
| New Caledonia | | | 850 | Face-centered cubic phase, very broad peaks | |
| | 49·3 | 4, * | | | Fig. 3 |
| Analytical data, | | | 950 | FCC phase clearer; olivine appears | |
| Part I, Tables 1, 3 | | | 1025 | Clear olivine pattern | |

https://doi.org/10.1346/CCMN.1973.0210108 Published online by Cambridge University Press

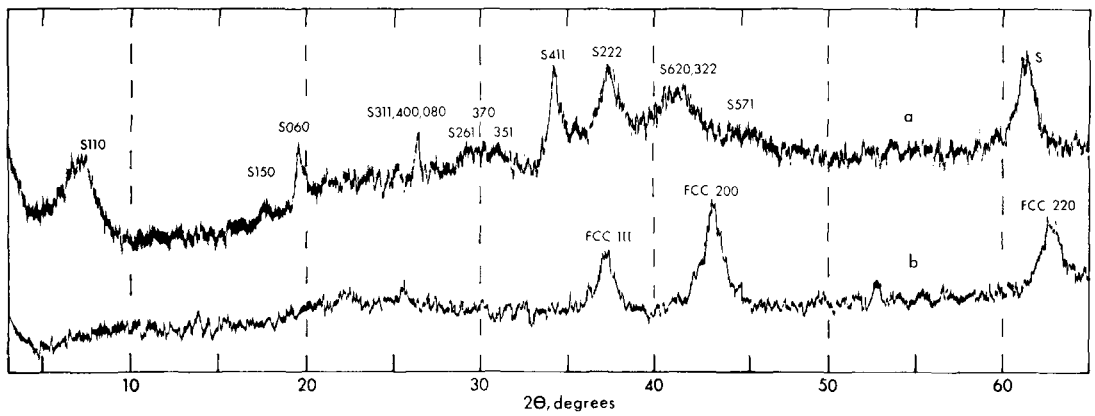



Fig. 2. Diffractometer patterns for sample Serbia 2, 27 wt % NiO estimated, after heating at (a) 800°C, (b) 1000°C; CuKα radiation. S = sepiolite, FCC = face-centered cubic (see text).

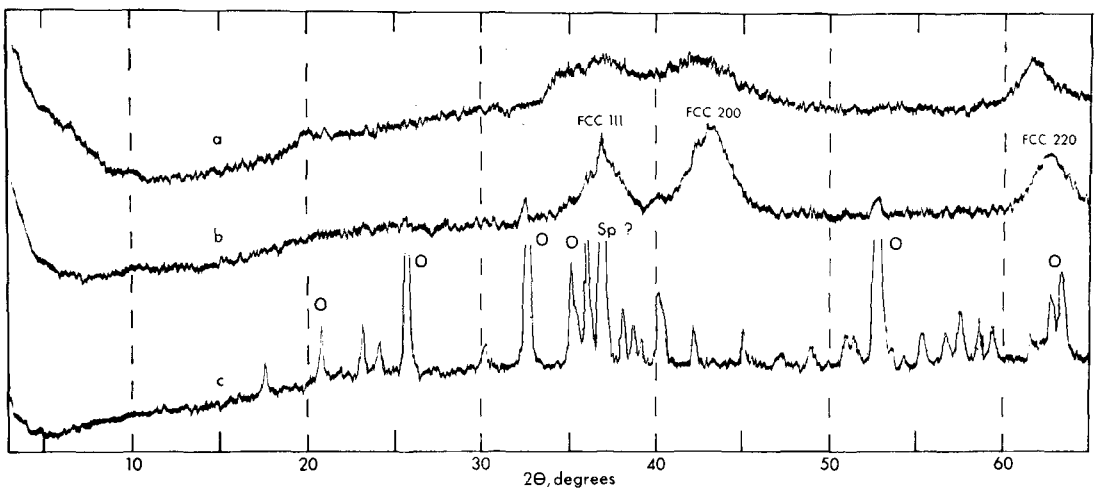



Fig. 3. Diffractometer patterns of a garnierite sample from New Caledonia, 49·3 wt % NiO, after heating at (a) 800°C, (b) 950°C, (c) 1025°C. Sp = possible spinel reflection or unusually strong olivine reflection, O = olivine, FCC = face-centered cubic (see text).

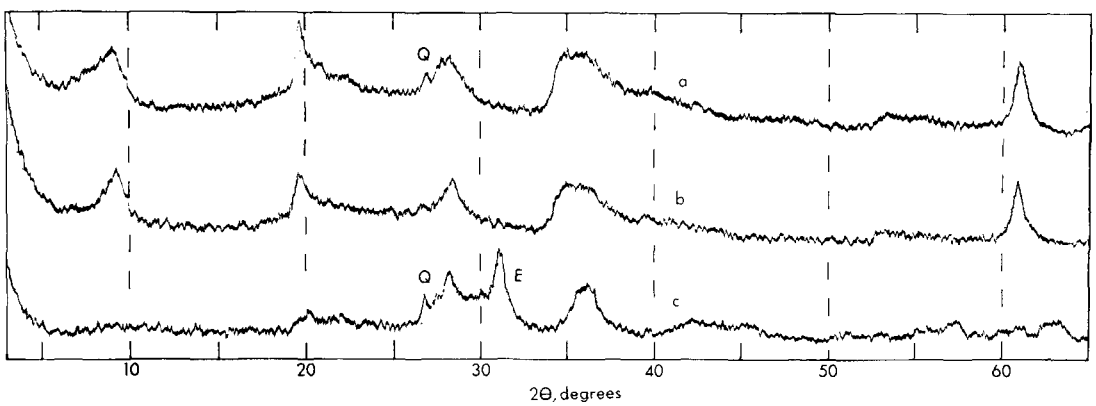



Fig. 4. Diffractometer patterns of a garnierite sample from N. Carolina, 5·5 wt % NiO, (a) at room temperature, (b) after 200°C, (c) after 800°C. Q = quartz, E = enstatite.

https://doi.org/10.1346/CCMN.1973.0210108 Published online by Cambridge University Press

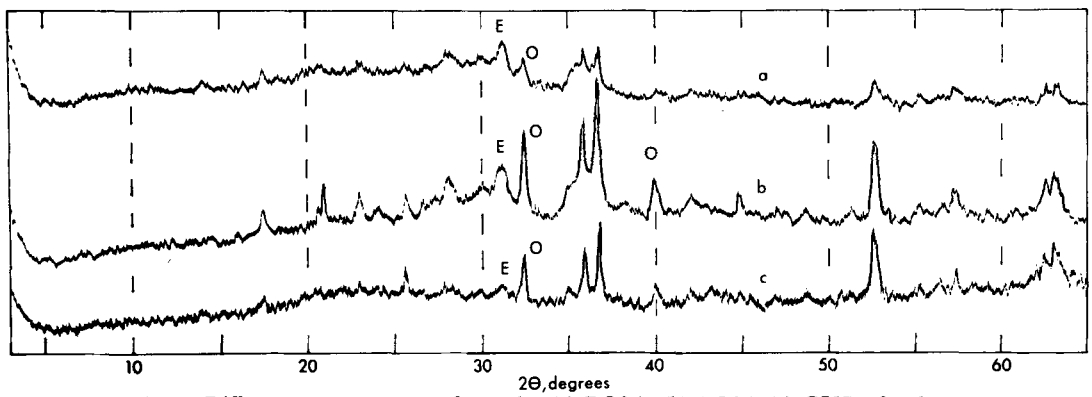



Fig. 5. Diffractometer patterns of samples (a) RO3A, (b) RO24, (c) GUS, after heat treatment at 1000°C. CuK$\alpha$ radiation. Q = quartz, E = enstatite, O = olivine.

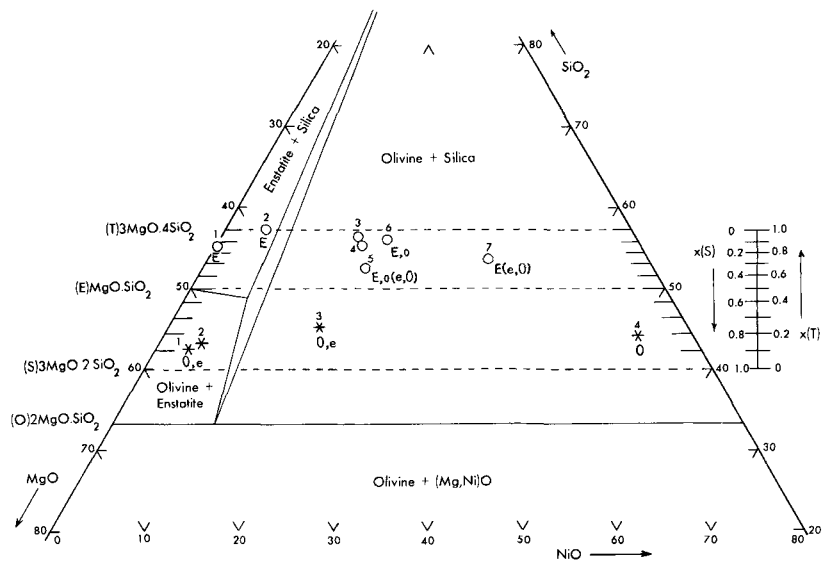



Fig. 6. Equilibrium diagram of MgO-NiO-$SiO_2$ system at 1400°C after Campbell and Roeder (1968), re-drawn on a mole percentage basis.

Garnierite composition points marked * for 7 Å-type and ○ for 10 Å-type. Numbers attached to composition points are explained in Tables 1 and 2. Analytical data plotted with $(Mg + 3/2\ R^{3+})$ in place of Mg.

Heating products at about 1000°C indicated by E, O for major enstatite-, major olivine-type products, and e, o for minor enstatite-, minor olivine-type products.

The scales $x(S)$ and $x(T)$ are described in the text.

between 550 and 800°C. With the lower NiO contents, (less than about 20 wt % NiO), a transformation to olivine occurs around 800°C together with a minor amount of enstatite. With higher NiO contents, olivine is not clearly seen until around 1000°C, and between 800° and 1000°C, transitional phases are observed, including in one case a sepiolite-like structure, and in three cases a face-centered cubic structure, with cubic parameter $a \simeq 4{\cdot}19$ Å, which is close to the values 4·213 Å for MgO and 4·178 Å for NiO. In one case, a reflection from a spinel-type structure may occur. The high-temperature phases, mainly olivine, are in accordance with the expected reactions, (see also Fig. 6).

*Talc-like, 10Å-type garnierites*

The results, summarized in Table 2 and illustrated in Figs. 4 and 5, show that little change occurs in the diffraction patterns until the temperature reaches 700–800°C. In this respect, the talc-

https://doi.org/10.1346/CCMN.1973.0210108 Published online by Cambridge University Press

Table 2. Summary of thermal transformations of 10 Å-type garnierites

| Sample | Wt % NiO | Composition Point in Fig. 6 | Temp. °C | X-ray diffraction data | |
|---|---|---|---|---|---|
| β-kerolite | 0·26 | 1, ○ | 20- | Initial pattern, with little change | |
| N. Carolina | 5·5 | 2, ○ | 700 | | |
| Analytical data, Part I, Table 2 | | | 800-1000 | Enstatite phase | Fig. 4 |
| Serbia 206 | ~ 25 | | 20- | Initial pattern, with little change | |
| Serbia 201 | ~ 39 | | 700 | | |
| Analytical data, Part I, Table 3 | | | 800-1000 | Enstatite phase, with trace of olivine phase | |
| RO24 | 19·6 | 5, ○ | 20- | Initial pattern, with little change | |
| RO3A | 20·8 | 6, ○ | 800 | | |
| GUS | 31·5 | 7, ○ | 850 | Enstatite, with minor olivine | Fig. 5 |
| Analytical data, Part, Table 2 | | | 1000 | Olivine, with minor enstatite | |

like garnierites differ from the serpentine-like forms in that a highly disordered phase extending over 200–250°C is not observed. Vitovskaya and Berkhin (1970) also made this observation. For low NiO contents, 0·26 and 5·5 wt %, an enstatite phase is obtained from 800–1000°C, without the appearance of olivine. For higher NiO contents, the results are somewhat conflicting. Two samples with estimated NiO contents of 25 and 39 wt % (full analyses of these samples were not made because of quartz impurities, and they are not represented in Fig. 6) gave mainly enstatite, with minor olivine in the range 800–1000°C. Three samples with NiO contents 19·6, 20·8 and 31·5 wt % also gave mainly enstatite and minor olivine at around 850°C, but major olivine and minor enstatite at around 1000°C.

These results are shown in the equilibrium diagram given in Figure 6. Enstantite as the main product with low NiO contents is the anticipated result. With higher NiO contents, the formation of olivine as the main product at 1000°C is in accordance with the equilibrium relations. The prior appearance of an enstatite phase probably represents an unstable product derived from the initial talc-like structure.

*Identification based on products formed up to* 1000°C

The present authors consider that the high temperature phases, particularly in the temperature range 800–1000°C, must be interpreted cautiously as regards their relation to the structural–chemical characteristics of the initial minerals.

A readily formed enstatite phase appears to be a clear indication of a low NiO content, talc-like form of garnierite. Vitovskaya and Berkhin (1968, 1970) drew a similar conclusion, though they used the term kerolite rather than garnierite. A minor amount of enstatite is difficult to interpret; it could arise either from a small proportion of a low NiO, talc-like form, or from a serpentine-like form transforming partly according to equation (1) rather than according to equation (3).

An olivine phase may develop in two ways. It is the normal major product from a serpentine-like garnierite up to about 1000°C. It also arises from high NiO, talc-like garnierites changing towards the equilibrium assemblage with olivine as the major product.

In Parts I and II of this study, it has been shown on the basis of chemical analyses and high-magnification electron micrographs that garnierites appear to be mixed crystallizations. It is of interest to consider these results in relation to the thermal transformation products. In Part I, the proportions of serpentine-like and talc-like components were calculated from the octahedral/tetrahedral cation ratios by assuming normal compositions for the components. Figure 6 shows two scales, marked $x(S)$ and $x(T)$, by which these proportions can be read directly from the position of a composition point in the triangular diagram. Thus, scale $x(S)$ gives the proportion of serpentine-like layers in a dominantly talc-type garnierite, and scale $x(T)$ the proportion of talc-like layers in a dominantly serpentine-like garnierite. However, whether these proportions exist as discrete phases, as interstratified layers, as defect structures, or as combinations for these possibilities, is very difficult to decide.

Among the serpentine-like garnierites, marked * in Fig. 6, point 3 (sample HMC5) has the highest

https://doi.org/10.1346/CCMN.1973.0210108 Published online by Cambridge University Press

calculated proportion of talc-like layers, 24 per cent. This sample shows minor enstatite at 1000°C, and this conceivably could have originated from a talc-like component. Among the talc-like garnierites, marked ○ in Fig. 6, numbers 5 and 7 have the highest calculated proportions of serpentine layers, respectively 36 and 27 per cent and these samples show prominent olivine at 1000°C. Admittedly olivine is expected in this area of the equilibrium diagram, but it is conceivable that the observed olivine originates in part from the apparently high proportions of serpentine-type layers.

Evidently it is very difficult to draw firm conclusions regarding the nature of particular garnierite samples from considerations of the thermal transformation products at 1000°C except when an enstatite phase alone appears.

*The transitional phases*

The 7 Å-type garnierites yielded particularly interesting results. In all cases, the initial structures became highly disordered around 550–600°C, when rapid loss of weight by dehydroxylation occurs (see Part I, Fig. 6a). Samples with the lowest NiO contents (MN6, 4·4; HMC5, 18·6 per-cent) transformed around 800°C into major olivine and minor enstatite. With greater NiO content, sample Serbia 2 (27 per cent NiO estimated) formed a sepiolite-like phase followed by a face-centered cubic phase before yielding mainly olivine around 1000°C. With high NiO content, samples from Kambalda and New Caledonia (respectively 43, 49 per cent NiO) gave a face-centered cubic phase around 850–950°C and mainly olivine near 1000°C.

The crystal structure of olivine approximates a hexagonal close-packed, (H.C.P.), oxygen anion arrangement. The structural transformation to the H.C.P. arrangement proceeded directly from the disordered dehydroxylate phase when the NiO content was small, but with more than 20 wt % NiO, a cubic close-packed (C.C.P.) anion arrangement formed in the temperature range 850–950°C. Presumably the difficulty of the conversion of the C.C.P. to the H.C.P. arrangement retarded the appearance of the olivine phase.

The formation of a sepiolite-like phase by sample Serbia 2, best developed at around 800°C, is an extraordinary result. It was indicated first by the formation of a diffraction peak (spacing) at around 12–13 Å, followed by all the more-clearly seen peaks of the normal sepiolite pattern. A similar low-angle peak has been observed in the thermal transformations of serpentine minerals (Nelson and Roy, 1954; Brindley and Zussman, 1957) mainly around 575–650°C, and the spacing ranged from about 15 Å–11 Å for different mineral specimens. The aluminum silicate, dickite, a two-layer, monoclinic member of the kaolinite mineral group, also has given a transitional 14 Å spacing (Hill, 1955, 1956; Roy and Brindley, 1956). None of these results is yet satisfactorily explained. The present example is the first in which a sepiolite crystallization has been seen. The existence of a Ni-containing sepiolite is already known (Hotz, 1964; especially 385–387), but this provides no explanation for the present result because no trace of sepiolite appears in the X-ray pattern of the initial mineral. The most that can be said at present is that these transitional phases represent ordered or semi-ordered stages in the process of structural re-organization. Vitovskaya and Berkhin (1970) remarked on the formation of a long spacing of about 22 Å when a 7 Å-type garnierite, 48 per cent NiO, was heated in the range 550–650°C, but gave no explanation; no similar observation has been made in the present studies.

## CONCLUSIONS

Serpentine-like and talc-like forms of garnierite transform at 800–1000°C largely according to their NiO content. With low NiO content, serpentine-like garnierites transform mainly to an olivine phase, and talc-like garnierites transform to an enstatite phase. With high NiO content, both forms of garnierite transform mainly to an olivine phase, though the talc-like form may give transitionally an enstatite phase. The use of these results to identify mixed crystallizations in the initial minerals is a very uncertain procedure.

Whereas serpentine-like garnierites give a 200–250°C temperature range in which a highly disordered phase appears accompanying the dehydroxylation reaction, talc-like garnierites transform at around 800°C to enstatite, or to olivine through transitional enstatite.

*Acknowledgments*—Thanks are tendered to the U.S. Agency for International Development (U.S.A.I.D.) for a scholarship to Pham Thi Hang, and to the Georgia Kaolin Company for a grant supporting the research program. The authors are endebted to many donors of mineral samples, who are thanked collectively for their assistance, and to Dr. Michael Fleischer and Miss Jaroslava Nigrin for making available translations of Russian articles.

## REFERENCES

Brindley, G. W. and Hayami, R. (1964) Kinetics and mechanisms of dehydration and recrystallization of serpentine—I and II: *Clays and Clay Minerals* **12**, 35–54.

Brindley, G. W. and Hayami, R. (1965) Mechanism of

https://doi.org/10.1346/CCMN.1973.0210108 Published online by Cambridge University Press

formation of forsterite and enstatite from serpentine: *Mineral. Mag.* **35**, 189–195.
Brindley, G. W. and Zussman, J. (1957) Structural study of the thermal transformation of serpentine minerals to forsterite: *Am. Mineral.* **42**, 461–474.
Campbell, F. E. and Roeder, P. (1968) The stability of olivine and pyroxene in the Ni-Mg-Si-O system: *Am. Mineral.* **53**, 257–268.
Hill, R. D. (1955) 14 Å spacings in kaolin minerals: *Acta Cryst.* **8**, 120.
Hill, R. D. (1956) Studies in rehydrated and refired kaolinite minerals. *Trans. Brit. Ceram. Soc.* **55**, 441–456.
Hotz, P. E. (1964) Nickeliferous laterites in southwestern Oregon and northwestern California. *Econ. Geol.* **59**, 355–396.
Nelson, B. W. and Roy, R. (1954) New data on the composition and identification of chlorites: *Clays and Clay Minerals* **2**, 335–348.
Roy, R. and Brindley, G. W. (1956) Hydrothermal reconstitution of the kaolin minerals: *Clays and Clay Minerals* **4**, 125–132.
Vitovskaya, I. V. and Berkhin, S. I. (1968) The problem of the nature of kerolite: *Kora Vyvetrivaniya* **10**, 134–159.
Vitovskaya, I. V. and Berkhin, S. I. (1970) The nature of garnierite. *Kora Vyvetrivaniya* **11**, 26–39.

**Résumé** – Les garniérites du type talc et serpentine décrites dans les parties I et II ont été chauffées à différentes températures jusqu'à 1000°C environ, et après chaque traitement ont été refroidies et examinées en diffraction X par diagramme de poudre. Les garniérites du type serpentine forment une phase hautement désordonnée à 550°C, température à laquelle une déshydroxylation rapide commence. Pour de basses teneurs en NiO (environ moins de 20 pour cent en poids) la phase désordonnée se transforme directement en une phase olivine autour de 800°C, mais, pour des teneurs en NiO plus élevées, diverses phases de transition se forment avant que n'apparaisse vers 1000°C une phase olivine. Une phase du type sépiolite a été obtenue avec un échantillon vers 800°C, et plusieurs échantillons ont montré des modifications du type cubique face centrée entre 900 et 1000°C.

Les garniérites du type talc avec de basses teneurs en NiO donnent une phase enstatite vers 800°C, qui suit immédiatement la réaction de déshydroxylation, mais pour les fortes teneurs en NiO, une phase olivine devient de plus en plus importante entre 850 et 1000°C. L'identification de cristallisations mixtes existant éventuellement dans les minéraux de départ est très difficile à faire sur la base des produits formés en chauffant jusqu'à 1000°C.

**Kurzreferat** – Die in den Teilen 1 und 2 beschriebenen serpentin- und talkartigen Garnieriten wurden auf verschiedene Temperaturen bis etwa 1000°C erhitzt und nach jeder Behandlung abgekühlt und in pulverförmigem Zustand nach dem Röntgenbeugungsverfahren untersucht. Die serpentinartigen Garnieriten bildeten bei etwa 550°C, wenn schnelle Dehydroxylation einsetzt, eine außerordentlich unregelmäßige Phase. Wenn der Gehalt an NiO gering war (etwa 20 Gew.-per cent) verwandelte sich diese Phase bei einer Temperatur von etwa 800°C unmittelbar in eine Olivinphase, doch bei höherem NiO Gehalt entstanden verschiedene Übergangsphasen, bevor bei etwa 1000°C eine Olivinphase auftrat. Bei einer Probe wurde im Bereich von 800°C eine sepiolitartige Phase erzielt, und mehrere Proben wiesen zwischen 900° und 1000°C würfelige Modifikationen an der Oberfläche auf.

Die talkartigen Garnieriten mit geringem NiO Gehalt bildeten eine Enstatitphase im Bereiche von 800°C unmittelbar nach der Dehydroxylationsreaktion, doch bei hohem NiO Gehalt trat zwischen 850° und 1000°C in immer höherem Baße eine Olivinphase in Erscheinung. Identifizierung der gemischten Kristallformen, die in den Ausgangsmineralien bestehen mögen, ist aufgrund der bis 1000°C gebildeten Produkte kaum durchführbar.

**Резюме** — Серпентино- и талькообразные гарниериты, описанные в частях I и II нагревались при различных температурах приблизительно до 1000°C и после каждой переработки охлаждались и исследовались рентгеновской дифракцией на порошке. При нагреве до 550°C, когда начинается быстрая гидроксиляция серпентинообразные гарниериты образовали очень беспорядочную фазу. При низком содержании NiO (приблизительно 20 вес %), беспорядочная фаза после нагрева до 800°C приблизительно менялась непосредственно в оливиновую фазу, но когда содержание NiO было более высоким, перед появлением оливиновой фазы при нагревании до 1000°C приблизительно формовались различные переходные фазы. С одной пробой получили сепиолитообразную фазу при нагреве до 800°C приблизительно, а на разных образцах заметили кубические изменения к центру поверхности при 900°–1000°C.

Талькообразные гарниериты с низким содержанием NiO формируют энстатитную фазу при 800°C приблизительно непосредственно после реакции дегидроксиляции, но при высоком содержании NiO оливиновая фаза становится более заметной при нагревании до 850°–1000°C. Идентификация смешанной кристаллизации, по всей вероятности, существующей в исходных минералах почти что невозможна на основании продуктов формующихся при нагревании до 1000°C.

https://doi.org/10.1346/CCMN.1973.0210108 Published online by Cambridge University Press