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.

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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 dehydroxy-
lation 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 increas-
ingly 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 use-
fullness 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–SiO2
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 Al2O3 and Fe2O3, in the natural mater-
ials and also because of the lower temperatures
used. The ternary diagram shows that Ni replaces
Mg in all proportions in the olivine phase.

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

\[
\text{Mg}_3 \text{Si}_2 \text{O}_7 (\text{OH})_4 \rightarrow \text{Mg}_2 \text{SiO}_4 + \text{Mg SiO}_3 + 2\text{H}_2\text{O}. \quad (1)
\]

\[
\text{Mg}_3 \text{Si}_4 \text{O}_{10} (\text{OH})_2 \rightarrow 3\text{Mg SiO}_3 + \text{SiO}_2 + \text{H}_2\text{O}. \quad (2)
\]

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):

\[
\text{Mg}_3 \text{Si}_2 \text{O}_5 (\text{OH})_4 \rightarrow (3/2) \text{Mg}_2 \text{SiO}_4 + (1/2) \text{SiO}_2 + 2\text{H}_2\text{O}. \quad (3)
\]

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

<table>
<thead>
<tr>
<th>NiO content</th>
<th>7Å-type, serpentine-like garnierite</th>
<th>10Å-type, talc-like garnierite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>Mainly olivine phase (equation 3), but possibly some enstatite (equation 2)</td>
<td>Enstatite phase (equation 2)</td>
</tr>
<tr>
<td>High</td>
<td>Olivine phase (equation 3 and phase diagram)</td>
<td>Olivine phase (phase diagram)</td>
</tr>
</tbody>
</table>

*Part I, by G. W. Brindley and Pham Thi Hang, discusses X-ray diffraction data, chemical analyses, theromgravimetric 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.
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 CuKα radiation, 1°(2θ)/min recording rate, 2–64°2θ).

The results are summarized in Tables 1 and 2, and illustrated in Figs. 1–5. Figure 6 reproduces 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+3/2R3+)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, 7 Å-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; CuKα radiation. Q = quartz, O = olivine, E = enstatite.](attachment:image.png)

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wt % NiO</th>
<th>Composition point in Temp.</th>
<th>X-ray diffraction data</th>
<th>Diffraction patterns</th>
</tr>
</thead>
<tbody>
<tr>
<td>MN6</td>
<td>4.4</td>
<td>1, *</td>
<td>600</td>
<td>Disordered phase formed; hk diffraction bands. Broad peak ~ 6°(2θ), 14–15 Å. Fig. 1</td>
</tr>
<tr>
<td>HMC5</td>
<td>18.6</td>
<td>3, *</td>
<td>800</td>
<td>Mainly olivine phase, minor enstatite</td>
</tr>
<tr>
<td>Analytical data, Part I, Table 1</td>
<td></td>
<td>1025</td>
<td>Mainly olivine, minor enstatite</td>
<td></td>
</tr>
<tr>
<td>Serbia 2</td>
<td>~ 27</td>
<td></td>
<td>500</td>
<td>Disordered phase formed Broad peak ~ 6°(2θ), 14–15 Å Sepiolite-like phase formed Prominent peak ~ 7.5°(2θ), 12 Å Fig. 2</td>
</tr>
<tr>
<td>Estimated NiO, Part I, Table 3</td>
<td></td>
<td></td>
<td>800</td>
<td>Face-centered cubic pattern</td>
</tr>
<tr>
<td>Kambalda</td>
<td>~ 42</td>
<td></td>
<td>550</td>
<td>Disordered phase formed</td>
</tr>
<tr>
<td>New Caledonia</td>
<td>49.3</td>
<td></td>
<td>850</td>
<td>Face-centered cubic phase, very broad peaks Fig. 3</td>
</tr>
<tr>
<td>Analytical data, Part I, Tables 1, 3</td>
<td></td>
<td></td>
<td>950</td>
<td>FCC phase clearer; olivine appears</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1025</td>
<td>Clear olivine pattern</td>
</tr>
</tbody>
</table>
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.
Fig. 5. Diffractometer patterns of samples (a) RO3A, (b) RO24, (c) GUS, after heat treatment at 1000°C. CuKa radiation. Q = quartz, E = enstatite, O = olivine.

Fig. 6. Equilibrium diagram of MgO-NiO-SiO2 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 O for 10 Å-type. Numbers attached to composition points are explained in Tables 1 and 2. Analytical data plotted with (Mg + 3/2 R3+) 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.

Talc-like, 10 Å-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-
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. Enstatite 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...
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.

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**REFERENCES**


Brindley, G. W. and Hayami, R. (1965) Mechanism of
THE NATURE OF GARNIERITES—III


Résumé—Les garnièrites 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 garnièrites du type serpentine forment une phase hautement désordonnée à 550°C, température à laquelle une déshydratation 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 garnièrites du type talc avec de basses teneurs en NiO donnent une phase enstatite vers 800°C qui suit immédiatement la réaction de déshydratation, 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.


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

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

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