

## THERMAL STABILITY AND OXIDATION OF $Mn_3O_4$ \*

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**ABSTRACT.** On the basis of thermal, X-ray, and infra-red investigations, it was found that  $Mn_3O_4$  heated in air within the thermal stability range of  $Mn_2O_3$  will be slowly oxidized to  $\alpha$ - $Mn_2O_3$  if it is pure; however, oxidation will be initiated and accelerated by the presence of other manganese oxides and also by ferric oxide. If the possibility of oxidation is excluded, as in  $N_2$  or  $CO_2$  atmosphere, the  $Mn_3O_4$  remains unchanged during prolonged heating in the temperature range cited above. However,  $Mn_2O_3$  heated in a  $CO_2$  atmosphere in its own thermal stability range will be decomposed into  $Mn_3O_4$  and even more  $MnO$  appears as a new phase. These experimental facts presumably may be used in interpreting the formation of manganese oxide assemblages in different metamorphic processes.

### INTRODUCTION

Thermal properties of artificial and natural manganese oxides, oxide hydrates, and manganese carbonate, as well as their transformations with increasing temperature were studied by several authors. The main results of these investigations were reviewed by SUPRIYA ROY [1972] in his paper about metamorphic manganese deposits.

It is well known — and therefore authors will not be cited here — that heated in air, different modifications of  $MnO_2$  transform at about 560 °C into  $\alpha$ - $Mn_2O_3$ , which in turn transforms by further increase of temperature, according to some authors at 870 °C, according to others at 950 °C, into low temperature (tetragonal)  $Mn_3O_4$ . It is also known that at 1050 °C [D. H. DASGUPTA, 1965] or at  $1160 \pm 5$  °C [J. J. VAN HOOK and M. L. KEITH, 1958] high temperature modification of  $Mn_3O_4$  forms.

The study of solubility and oxidation of different manganese compounds, in the first line of manganese carbonate, as a function of pH and Eh of aqueous solutions is of great importance for interpreting the conditions of formation of supergene manganese oxide deposits. Similar importance is, however, to be attributed to studying thermal properties and transformations of manganese oxides from the point of view of formation of metamorphic manganese deposits.

As generally known,  $Mn_3O_4$  is the stable oxide of manganese at higher temperatures above about 940 °C, i.e. the different manganese oxides and oxide hydrates transform into  $Mn_3O_4$  at that temperature. Less data are found, however, in the related literature concerning the range of temperature and the conditions in which

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the stability of  $Mn_3O_4$  really exists. As the authors dealing with the metamorphism of manganese deposits point out, both chemical and mineral composition of the mineral assemblage formed during the metamorphism are strongly influenced by  $f_{CO_2}$  and  $f_{O_2}$  as well as by temperature and pressure and by the initial chemical and mineral composition of the metamorphized sediment.

The question arises, therefore, whether the  $Mn_3O_4$  corresponding to hausmannite, at temperatures lower than its temperature of formation, shows changes to be taken into consideration in interpreting the formation of metamorphic manganese deposits.

## OXIDATION OF $Mn_3O_4$

### *Oxidation in aqueous medium*

References concerning oxidation of  $Mn_3O_4$  in aqueous, slightly acidic media are to be found in the paper of several authors, such as MOTOAKI SATO [1955] and O. BRICKER [1966]. According to BRICKER during prolonged oxidation in slightly acidic aqueous medium the cinnamon brown colour of  $Mn_3O_4$  became darker and, though the X-ray pattern remained the same as characteristic for  $Mn_3O_4$ , the grade of oxidation of the product proved to be  $MnO_{1.44}$ . BRICKER and HUEBNER [1969] similarly suppose that, during the oxidation mentioned above,  $\gamma$ - $Mn_2O_3$  was formed, the X-ray pattern of which cannot be distinguished from that of hausmannite.

Unpublished results [1964] of the present author support the above statements with the addition that, in strongly acidic medium and at higher temperatures, the oxidation of  $Mn_3O_4$  does not end at the grade of oxidation  $MnO_{1.5}$  corresponding to  $Mn_2O_3$ , but approaches that of  $MnO_2$ . According to our investigations, the same situation is found to be valid in the case of  $\alpha$ - $Mn_2O_3$  treated with strongly acidic solutions at higher temperatures.

In strongly acidic medium (pH=1) and at higher temperatures (40—60 °C) the oxidation was very intensive, and the grade of oxidation of the  $Mn_3O_4$  treated reached  $MnO_{1.437}$  after 3 hours, rose to  $MnO_{1.659}$  after 10 hours and to  $MnO_{1.70}$  after 24 hours. The water content increased almost linearly with the grade of oxidation from 0.57% to 3.86% after 5 hours and to 4.37% after 24 hours. The oxidation at pH=1 and 25 °C is also definite, but its rate is lower; the grade of oxidation of  $Mn_3O_4$  was  $MnO_{1.44}$  after 24 hours treatment, and the water content reached 3.56%. A similar behaviour was found with  $\alpha$ - $Mn_2O_3$ , however, with a slower increase in grade of oxidation and water content.

The progress in time of the oxidation of  $Mn_3O_4$  treated at 60 °C in a solution of pH=1 could be well followed by IR-spectroscopic investigation of the products. While the spectrum of the sample treated 3 hours corresponded to that of  $Mn_3O_4$ , after 9 hours, and even more after 24 hours treatment, the spectra of the samples ceased to show the characteristics of  $Mn_3O_4$ ; neither did the characteristic absorption bands of  $\alpha$ - $Mn_2O_3$  appear, the spectrum resembled much more to the IR-spectrum of a cryptomelane species from Urkut (Hungary) or to that of an artificial  $\gamma$ - $MnO_2$ .

### *Oxidation at higher temperatures*

Oxidation of  $Mn_3O_4$  between 250—550 °C in nitrogen-oxygen mixture (0—100% oxygen) is mentioned by H. R. OSWALD and M. J. WAMPETICH [1967]. According to these authors, in the oxidation of the small hausmannite grains an oxide of

$Mn_3O_8$  ( $MnO_{1.60}$ ) composition is formed as a transitional step, which transforms into  $\alpha$ - $Mn_2O_3$  above 550 °C.

The author [GY. GRASSELLY and É. KLIVÉNYI, 1956*a*, 1956*b*] called the attention to the fact, supported also by the present investigations and the results of the authors mentioned above that, though  $Mn_3O_4$  is really the stable oxide of manganese above 940 °C, however, heated in air in the temperature range of stability of  $\alpha$ - $Mn_2O_3$ , it is oxidized into  $\alpha$ - $Mn_2O_3$  in the presence of other manganese oxides.

The dependence on temperature and time of the oxidation of  $Mn_3O_4$  into  $\alpha$ - $Mn_2O_3$  can be especially well followed by thermal investigations. The initial temperature of oxidation, the beginning of the decomposition into  $Mn_3O_4$  of the  $\alpha$ - $Mn_2O_3$  formed during the former oxidation and the end of this retransformation, as well as the increase and the decrease in weight due to these changes can be especially well read from the TGA curves. Knowing the grade of oxidation, i.e. the composition of the starting material, the grade of oxidation belonging to different temperatures can be calculated from the data of TGA curves.

### RESULTS OF THERMAL INVESTIGATIONS

Thermal investigations were performed with ERDEY-PAULIK'S "Derivatograph"; the heating rate was 10 °C/min. The instrument permits to record T, TGA, DTGA and DTA curves contemporaneously. From these, TGA curves obtained with uniform heating are presented in Figs. 1 and 2, while Fig. 3 shows TGA curves during prolonged heating at constant temperature 650–670 °C.

In Fig. 1, curves A, B and C are TGA curves of the same  $Mn_3O_4$  sample obtained by heating over 1000 °C, but with different rates of cooling of the products. In the case of curve A, the sample was cooled slowly in a closed furnace after several hours ignition at 1050 °C; for curve B the cooling period was shorter than for curve A, while in the case of curve C it occurred in a comparatively short time. The rate of oxidation decreased in the order of the curves A, B, C: the slower the cooling of the  $Mn_3O_4$  formed by ignition above 1000 °C was, the higher the quantities of  $Mn_3O_4$  transformed into  $\alpha$ - $Mn_2O_3$  between 600–800 °C; resulting an increase in weight which can be seen from the TGA curve. It can also be stated that the less the admixture of  $\alpha$ - $Mn_2O_3$  to the  $Mn_3O_4$  is, the higher the temperatures at which the oxidation starts: in curve A already at 500 °C, in curve B at 600 °C and in curve C at about 700 °C. As starting material for further investigations, this  $Mn_3O_4$  sample was used.

The question may arise, how the oxidation of  $Mn_3O_4$  is influenced by other manganese compounds present.

The answer to this question can be found in the TGA curves shown in Fig. 1, 2 and 3.

In Fig. 1, beside the TGA curves of the  $Mn_3O_4$  samples mentioned above those of  $Mn_3O_4$  samples containing 1% of  $\beta$ - $MnO_2$ ,  $\gamma$ - $MnO_2$  and  $\eta$ - $MnO_2$ , respectively, are presented, with the starting temperature of oxidation. The grade of oxidation calculated from the TGA curves at 650–660 °C is also given, as well as that for the temperature 870–880 °C at which the decomposition of  $\alpha$ - $Mn_2O_3$  formed by oxidation of  $Mn_3O_4$  begins.

On the basis of TGA curves of Fig. 1 the following statements can be made:

a) While in the TGA curve of the comparatively pure  $Mn_3O_4$  only oxidation of negligible degree can be seen, the oxidation of  $Mn_3O_4$  to  $\alpha$ - $Mn_2O_3$  in the thermal

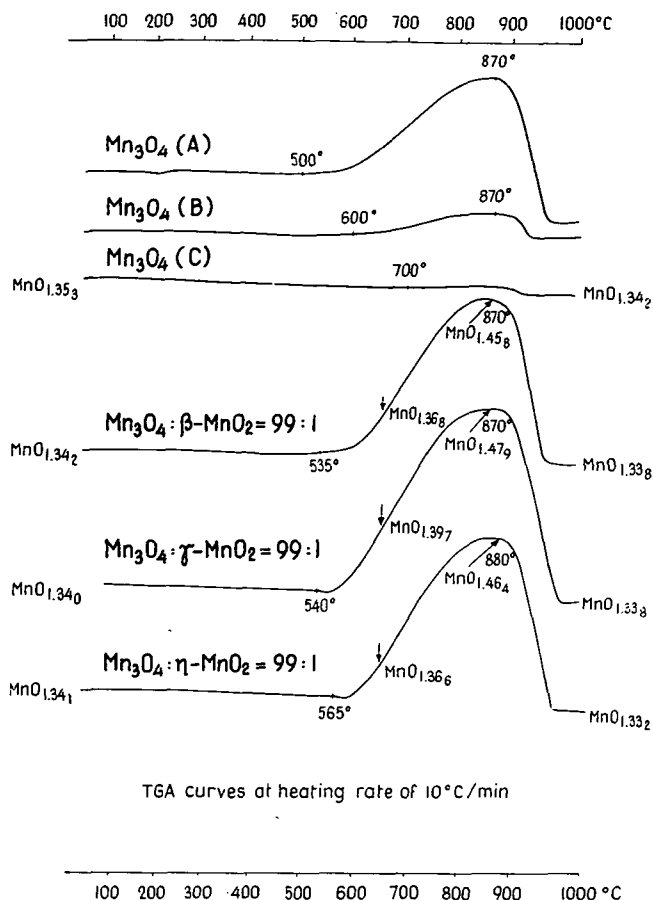


Fig. 1. TGA curves of  $\text{Mn}_3\text{O}_4$  and mixtures of  $\text{Mn}_3\text{O}_4$  with  $\text{MnO}_2$ -modifications heated in air with 10°C/min rate (see the text)

stability range of the latter is significantly accelerated by adding 1%  $\text{MnO}_2$ -modification to the  $\text{Mn}_3\text{O}_4$ .

b) The starting temperature of the oxidation seems to be influenced by the character of the  $\text{MnO}_2$ ; the oxidation starts at a substantially lower temperature — depending on the  $\text{MnO}_2$ -modification present — than that of pure  $\text{Mn}_3\text{O}_4$ .

c) The most intensive effect on the oxidation of  $\text{Mn}_3\text{O}_4$  was exerted by  $\gamma$ - $\text{MnO}_2$ .

d) With the heating rate 10°C/min used the product at 870–880°C approximates fairly well the composition  $\text{MnO}_{1.50}$  corresponding to  $\alpha$ - $\text{Mn}_2\text{O}_3$ , though to reach this composition a more prolonged heating would be necessary.

Thus, with the heating rate mentioned the predominant part of the  $\text{Mn}_3\text{O}_4$  was oxidized to  $\alpha$ - $\text{Mn}_2\text{O}_3$  up to 870°C.

e) At this temperature the transformation of the  $\text{Mn}_2\text{O}_3$  into  $\text{Mn}_3\text{O}_4$  begins. As can be seen from the TGA curves, this process is faster (the corresponding section of the curve is steeper) than the preceding oxidation. The transformation

into  $Mn_3O_4$  occurs between 870—970 °C, the rate of the reaction being the highest at about 940—950 °C. The composition of the resulting  $Mn_3O_4$  (after rapid cooling) is near to the ideal  $MnO_{1.33}$ .

In Fig. 2 beside the TGA curves of the starting  $Mn_3O_4$  and of  $\alpha-Mn_2O_3$  and curves of different mixtures of both materials, as well as those of samples contain 1% manganite and  $Fe_2O_3$ , respectively, are shown. Similarly as in Fig. 1, the starting temperatures of oxidation and the grades of oxidation reached at 650—660 °C and about 860—870 °C are indicated.

The TGA curves of Fig. 2 permit the following statements:

a) By comparing the TGA curve of pure  $Mn_3O_4$  with those of the mixtures it can be seen that the oxidation of  $Mn_3O_4$  is significantly accelerated by the presence of other manganese oxides in the temperature range 500—870 °C.

b) The starting temperature of oxidation depends on quality and quantity of the material added to  $Mn_3O_4$ . In the presence of 50%  $\alpha-Mn_2O_3$  the oxidation begins at about 460 °C, with 1%  $\alpha-Mn_2O_3$  at about 490 °C, while in the presence

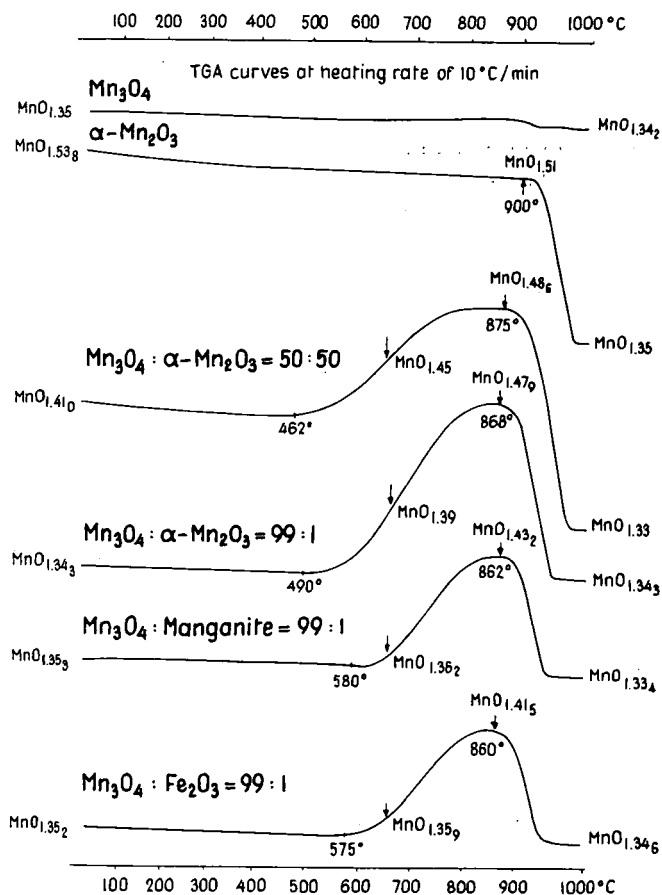


Fig. 2. TGA curves of  $Mn_3O_4$ ,  $Mn_2O_3$  and mixtures of  $Mn_3O_4 - \alpha-Mn_2O_3$ ,  $Mn_3O_4 - \text{manganite}$  and  $Mn_3O_4 - Fe_2O_3$  heated in air (see the text)

of manganite and  $\text{Fe}_2\text{O}_3$  the starting temperature of oxidation is between 570—580 °C.

c) The most intensive effect on the oxidation of  $\text{Mn}_3\text{O}_4$  is exerted by  $\alpha\text{-Mn}_2\text{O}_3$ , the oxidation being more intensive than in presence of other compounds,  $\text{MnO}_2$  included.

d) With the given heating rate the oxidation terminates at 860—870 °C and the grade of oxidation at this temperature is more or less near to the composition of  $\text{Mn}_2\text{O}_3$  depending on the material added. At the same temperature the retransformation into  $\text{Mn}_3\text{O}_4$  begins.

e) The composition of the  $\text{Mn}_3\text{O}_4$  formed as endproduct (with rapid cooling) is near to the ideal also in this case

In Fig. 3 TGA curves of  $\text{Mn}_3\text{O}_4$  samples containing  $\gamma\text{-MnO}_2$  (curve A) and  $\alpha\text{-Mn}_2\text{O}_3$  (curves B, C, D) in the concentrations indicated as well as those of comparatively pure  $\text{Mn}_3\text{O}_4$  samples, rapidly cooled after heating, (curves E, F) are presented.

Up to the temperature indicated (500 °C, 660—670 °C and 650 °C, respectively) the heating rate was 10 °C/min, then the heating was pursued at the same temperature for 3 hours. On the TGA curves the composition calculated from the increase in weight at the given temperature is indicated (irrespective of the material being not monophase) as well as the composition (grade of oxidation) reached after 1, 2 and 3 hours.

From the TGA curves of Fig. 3 the following conclusions can be drawn:

a) In DTA and TGA investigations with the heating rate generally used (here 10 °C/min), the possible oxidation may be overlooked (Fig. 1, curve C) because no significant changes can be observed neither in the DTA nor in the TGA curves. This is comprehensible, namely the oxidation of  $\text{Mn}_3\text{O}_4$  to  $\alpha\text{-Mn}_2\text{O}_3$  is not an instantaneous reaction, the rate of which being possible influenced by several factors. Therefore, even if no oxidation is observed in the usual DTA-TGA investigation, by heating the sample at a given temperature for a shorter or longer time the fact of the oxidation will become evident.

Curves E and F of Fig. 3 are TGA curves of two relatively pure  $\text{Mn}_3\text{O}_4$  samples heated at 650 °C for 3 hours. DTA and TGA curves of these samples with normal heating rate showed practically no changes. At the same time heating the samples at 650 °C, the oxidation begins and after 3 hours the grade of oxidation of both  $\text{Mn}_3\text{O}_4$  samples reaches approximately the value  $\text{MnO}_{1.46}$ , though it is perceivable that the oxidation has not been finished during the time.

b) The initiating and accelerating effect exerted on the oxidation of  $\text{Mn}_3\text{O}_4$  by other manganese oxides can be well observed by comparing the curves A to D and E, F. The  $\text{Mn}_3\text{O}_4$ , the oxidation of which begins only slowly at 650 °C and which reaches the grade of oxidation  $\text{MnO}_{1.38}$  after 1 hour in pure state, with admixture of 1% of other manganese oxides will exceed this value at the moment of reaching the temperature 650—660 °C and after 1 hour the grade of oxidation will be almost stabilized with the value  $\text{MnO}_{1.48}$ .

c) According to Fig. 2 the oxidation of the mixture 99%  $\text{Mn}_3\text{O}_4$  — 1%  $\alpha\text{-Mn}_2\text{O}_3$  starts at 490—500 °C. This temperature does not belong to the thermal stability range of  $\alpha\text{-Mn}_2\text{O}_3$ , being under the lower limit of the latter. The oxidation of the mixture begins, however, at this temperature (curve D), though the process is slow and the grade of oxidation rises only to  $\text{MnO}_{1.39}$  after 3 hours. Heating the sample for a suitable period of time would evidently lead to complete oxidation of the  $\text{Mn}_3\text{O}_4$  even at 500 °C.

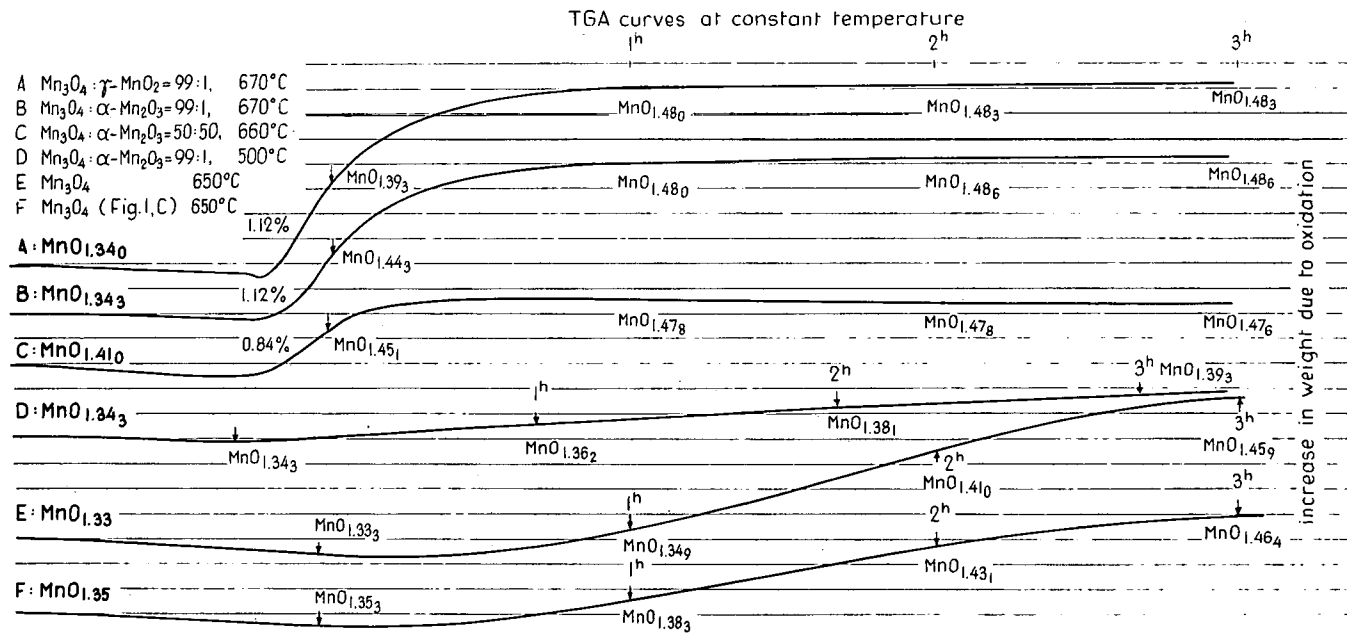


Fig. 3. TGA curves of  $\text{Mn}_3\text{O}_4$  —  $\gamma$ - $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$  —  $\alpha$ - $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  samples during prolonged heating at constant temperature (see the text).

RESULTS OF INFRARED SPECTROSCOPIC  
AND X-RAY INVESTIGATIONS

The oxidation of  $Mn_3O_4$  in air between 500 and 800 °C as well as that accelerated by other manganese oxides of higher valency is supported by qualitative investigations with IR-spectroscopy and X-ray, too.

IR-spectra were recorded with a Zeiss UR-20 spectrophotometer in the spectral range 400—800  $cm^{-1}$ . X-ray patterns were obtained with an X-ray diffractometer DRON-1 with Fe  $K_{\alpha}$  radiation (30 kV, 10 mA). Both in the IR-spectra and in the X-ray patterns the evanescence of the characteristics of  $Mn_3O_4$  and the coming into prominence of the bands of  $\alpha-Mn_2O_3$  can be well followed in its dependence on the time of heating.

As can be seen from the X-ray patterns, the intensity of the reflexions characteristic for  $Mn_3O_4$  begins to decrease in the samples heated to 660 °C, then with prolonged heating the reflexions of  $\alpha-Mn_2O_3$  become more and more dominant, though the presence of some  $Mn_3O_4$  can be observed even after heating for 3 hours. The oxidation of  $Mn_3O_4$  to  $\alpha-Mn_2O_3$  could not be considered as complete on the basis of TGA curves.

TABLE I

*d*(Å)-values of the starting material 99%  $Mn_3O_4$ —1%  $\alpha-Mn_2O_3$  and those of sample heated to 660 °C, after 1 hour and 3 hours

<i>d</i> (Å)	Phase	<i>I</i> <sub>estim</sub>			
		starting material	samples heated at 660 °C for		
			0 <sup>h</sup>	1 <sup>h</sup>	3 <sup>h</sup>
4.88	$Mn_3O_4$	m	m	—	—
3.84	$\alpha-Mn_2O_3$	—	w	s	s
3.07	$Mn_3O_4$	m	m	—	—
2.86	$Mn_3O_4$	m	w	—	—
2.76	$Mn_3O_4$	vs	s	vw	—
2.74	$\alpha-Mn_2O_3$	—	s	vs	vs
2.47	$Mn_3O_4$	vs	s	w	vw
2.35	$\alpha-Mn_2O_3$	m	m	m	m
	$Mn_3O_4$				
2.02	$Mn_3O_4$	m	m	—	m
1.98	$\alpha-Mn_2O_3$	—	w	m	m
1.84	$\alpha-Mn_2O_3$	—	w	m	m
1.78	$Mn_3O_4$	—	m	—	—

The IR-spectra are also in full accordance with the results of TGA and X-ray investigations.

Comparing curves 3 to 6 of Fig. 4, it is evident that, while the absorption band at 670  $cm^{-1}$  characteristic for  $\alpha-Mn_2O_3$  appears already in the spectrum of the sample heated to 670 °C and rapidly cooled, this band becomes more and more intensive after 1 hour and 3 hours treatment; curve 4 is more similar to the spectrum of the starting mixture, the characteristics of  $\alpha-Mn_2O_3$  become more and more conspicuous in curves 5 and 6.

The same is valid in the case of the 50—50 % mixture. The starting mixture shows the characteristics of both components. The IR-spectra of the samples heated



TABLE 2

$d(\text{\AA})$ -values of the starting material 50%  $\text{Mn}_3\text{O}_4$  — 50%  $\alpha\text{-Mn}_2\text{O}_3$  and those of sample heated to 660 °C, after 1 hour and 3 hours heating in air

$d(\text{\AA})$	Phase	$I_{\text{estim}}$			
		starting material	samples heated at 660 °C for		
			0 <sup>h</sup>	1 <sup>h</sup>	3 <sup>h</sup>
4.88	$\text{Mn}_3\text{O}_4$	m	vw	vw	vw
3.84	$\alpha\text{-Mn}_2\text{O}_3$	m	s	s	s
3.07	$\text{Mn}_3\text{O}_4$	m	vw	—	—
2.86	$\text{Mn}_3\text{O}_4$	w	vw	—	—
2.76	$\text{Mn}_3\text{O}_4$	vs	m	—	—
2.72	$\alpha\text{-Mn}_2\text{O}_3$	vs	vs	vs	vs
2.47	$\text{Mn}_3\text{O}_4$	vs	m	vw	vw
2.35	$\text{Mn}_3\text{O}_4$				
2.35	$\alpha\text{-Mn}_2\text{O}_3$	m	m	s	s
2.02	$\text{Mn}_3\text{O}_4$	m	vw	—	—
1.98	$\alpha\text{-Mn}_2\text{O}_3$	m	m	s	s
1.84	$\alpha\text{-Mn}_2\text{O}_3$	m	m	s	s
1.78	$\text{Mn}_3\text{O}_4$	m	vw	—	—

to 660 °C (curve 8), and those of samples treated at that temperature for 1 and 3 hours (curves 9 and 10) become more and more similar to the IR-spectrum characteristic for  $\alpha\text{-Mn}_2\text{O}_3$  (curve 2).

#### BEHAVIOUR OF $\text{Mn}_3\text{O}_4$ AT HIGHER TEMPERATURES IN $\text{CO}_2$ AND $\text{N}_2$ ATMOSPHERE

To obtain further information on the behaviour of  $\text{Mn}_3\text{O}_4$ , the behaviour of the starting materials consisting of  $\text{Mn}_3\text{O}_4$  and  $\alpha\text{-Mn}_2\text{O}_3$ , as well as different mixtures of both was investigated in  $\text{CO}_2$  and  $\text{N}_2$  atmosphere, too, after heating the samples at 670 °C in the atmosphere indicated for 2 or 3 hours and then cooling in  $\text{CO}_2$  or  $\text{N}_2$  stream. We intend to continue these investigations in the future.

Some results are presented in Fig. 5. On the left of Fig. 5 the IR-spectra of  $\text{Mn}_3\text{O}_4$  and  $\alpha\text{-Mn}_2\text{O}_3$  as starting materials and of different mixtures of both, as well as the spectra of the products obtained from  $\alpha\text{-Mn}_2\text{O}_3$  by heating at 670 °C or 2 hours are to be seen.

The  $\text{Mn}_3\text{O}_4$  heated in  $\text{CO}_2$  stream at 670 °C for 2 hours shows no changes, its spectrum is nearer to that of ideal  $\text{Mn}_3\text{O}_4$  than the spectrum of the starting material. In contrary heating  $\alpha\text{-Mn}_2\text{O}_3$  and mixtures containing  $\alpha\text{-Mn}_2\text{O}_3$  in  $\text{CO}_2$  stream at the given temperature more substantial changes are observed. The spectrum characteristic for  $\alpha\text{-Mn}_2\text{O}_3$  disappears and it is substituted by that characteristic for  $\text{Mn}_3\text{O}_4$ . While by heating in air between 600 and 800 °C the  $\text{Mn}_3\text{O}_4$  was oxidized into  $\alpha\text{-Mn}_2\text{O}_3$ , during heating in  $\text{CO}_2$  atmosphere the  $\text{Mn}_3\text{O}_4$  remains unchanged and  $\alpha\text{-Mn}_2\text{O}_3$  transforms into  $\text{Mn}_3\text{O}_4$ . It is to be remarked that the endproducts obtained by heating both  $\alpha\text{-Mn}_2\text{O}_3$  and its mixtures in  $\text{CO}_2$  stream are heterogenous according to X-ray investigations; with reflexions of the dominating  $\text{Mn}_3\text{O}_4$  as a rest those of  $\alpha\text{-Mn}_2\text{O}_3$  are to be seen; even MnO appears as a new phase, especially

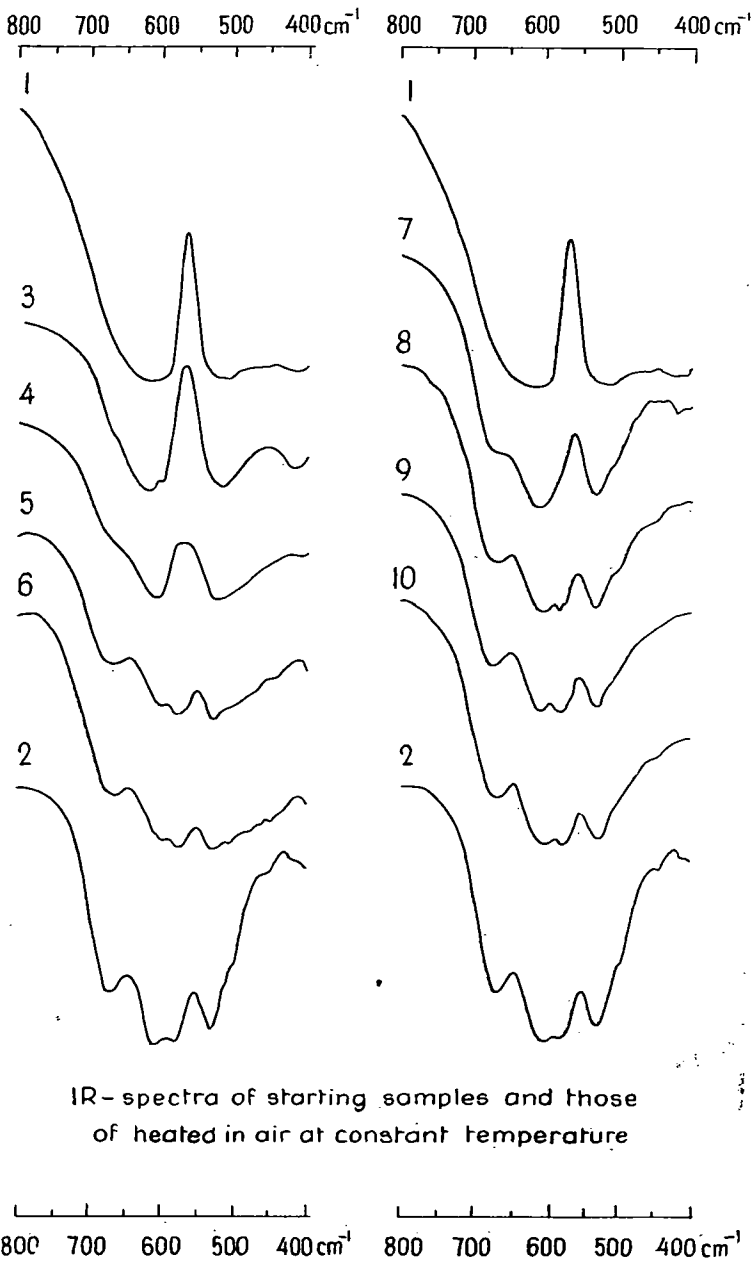


Fig. 4. IR-spectra of the starting materials and of samples heated to 660–670 °C in air: 1.  $Mn_3O_4$ , 2.  $\alpha-Mn_2O_3$ , 3. 99 %  $Mn_3O_4$  — 1%  $\alpha-Mn_2O_3$ , 4. The same as 3, heated to 670 °C, 5–6. The same sample heated at 670 °C for 1 hour and 3 hours, respectively. 7. 50%  $Mn_3O_4$  — 50%  $\alpha-Mn_2O_3$ , 8. The same as 7, heated to 660 °C, 9–10. The same sample heated at 660 °C for 1 hour and 3 hours, respectively.

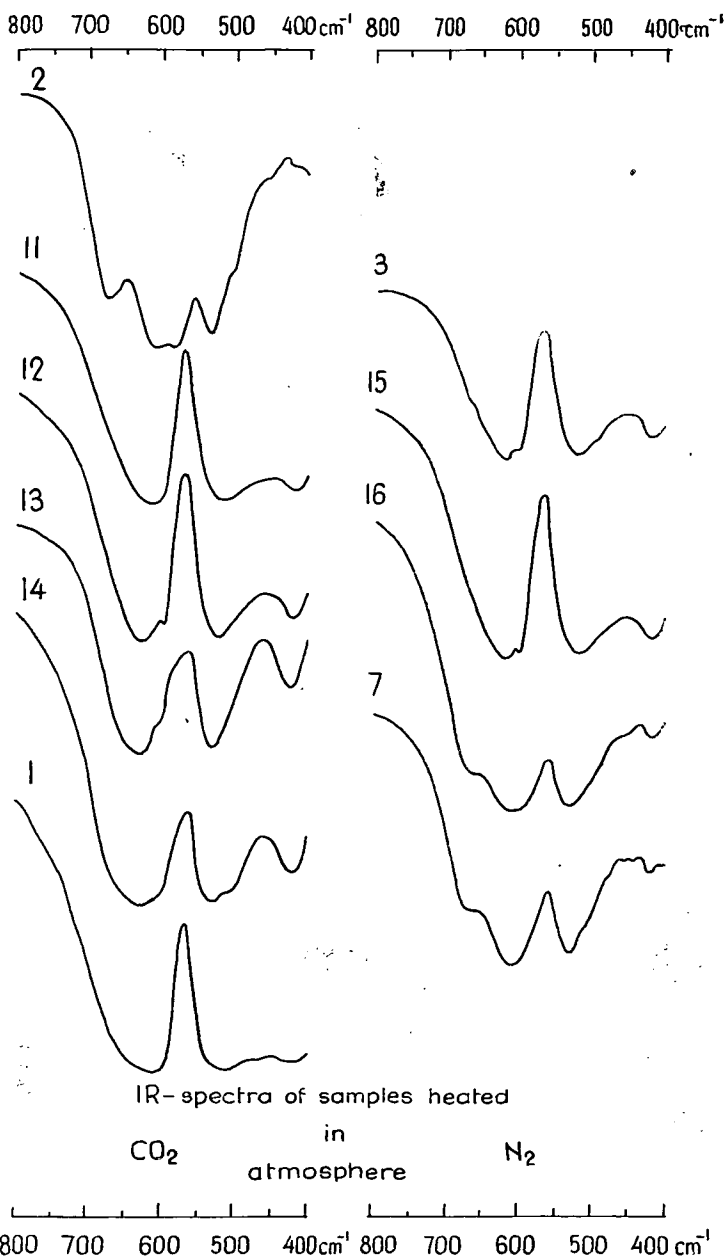


Fig. 5. IR-spectra of different starting materials and of samples heated to 660–670 °C in CO<sub>2</sub> or N<sub>2</sub> atmosphere:

Untreated samples: 1. Mn<sub>3</sub>O<sub>4</sub>, 2. α-Mn<sub>2</sub>O<sub>3</sub>, 3. 99% Mn<sub>3</sub>O<sub>4</sub> — 1% α-Mn<sub>2</sub>O<sub>3</sub>, 7. 50% Mn<sub>3</sub>O<sub>4</sub> — 50% α-Mn<sub>2</sub>O<sub>3</sub>;

Samples heated in CO<sub>2</sub> atmosphere:

1. Mn<sub>3</sub>O<sub>4</sub>, 12. 75% Mn<sub>3</sub>O<sub>4</sub> — 25% α-Mn<sub>2</sub>O<sub>3</sub>, 13. α-Mn<sub>2</sub>O<sub>3</sub>, 14. 25% Mn<sub>3</sub>O<sub>4</sub> — 75% α-Mn<sub>2</sub>O<sub>3</sub>;

Samples heated in N<sub>2</sub> atmosphere:

15. 99% Mn<sub>3</sub>O<sub>4</sub> — 1% α-Mn<sub>2</sub>O<sub>3</sub>, 16. 50% Mn<sub>3</sub>O<sub>4</sub> — 50% α-Mn<sub>2</sub>O<sub>3</sub>.

TABLE 3

*d*-values of samples heated at 670 °C in CO<sub>2</sub> atmosphere for 2 hours

<i>d</i> (Å)	Phase	$\alpha$ -Mn <sub>2</sub> O <sub>3</sub>	75% Mn <sub>3</sub> O <sub>4</sub> 25% Mn <sub>2</sub> O <sub>3</sub>	25% Mn <sub>3</sub> O <sub>4</sub> 75% Mn <sub>2</sub> O <sub>3</sub>	Mn <sub>3</sub> O <sub>4</sub>
4.88	Mn <sub>3</sub> O <sub>4</sub>	m	m	w	m
3.84	$\alpha$ -Mn <sub>2</sub> O <sub>3</sub>	—	—	m	—
3.07	Mn <sub>3</sub> O <sub>4</sub>	s	s	m	m
2.86	Mn <sub>3</sub> O <sub>4</sub>	w	w	vw	vw
2.74	Mn <sub>3</sub> O <sub>4</sub>	vs	vs	s	vs
2.72	$\alpha$ -Mn <sub>2</sub> O <sub>3</sub>	—	—	vs	—
2.56	MnO	s	vw	vw	—
2.47	Mn <sub>3</sub> O <sub>4</sub>	vs	vs	vs	vs
2.35	Mn <sub>3</sub> O <sub>4</sub>	w	w	w	w
	$\alpha$ -Mn <sub>2</sub> O <sub>3</sub>				
2.22	MnO	vs	vw	w	—
2.02	Mn <sub>3</sub> O <sub>4</sub>	w	m	w	w
1.98	$\alpha$ -Mn <sub>2</sub> O <sub>3</sub>	—	—	w	—
1.82	Mn <sub>3</sub> O <sub>4</sub>	vw	vw	w	vw
1.78	Mn <sub>3</sub> O <sub>4</sub>	w	w	w	—
Composition of the samples	at the start	MnO <sub>1.53</sub>	MnO <sub>1.38</sub>	MnO <sub>1.46</sub>	MnO <sub>1.35</sub>
	after heating	MnO <sub>1.24</sub>	MnO <sub>1.33</sub>	MnO <sub>1.37</sub>	MnO <sub>1.25</sub>

TABLE

*d*-values of samples heated in N<sub>2</sub> atmosphere at 670 °C for 3 hours

<i>d</i> (Å)	Phase	50% Mn <sub>3</sub> O <sub>4</sub> + 50% Mn <sub>2</sub> O <sub>3</sub>		99% Mn <sub>3</sub> O <sub>4</sub> + 1% Mn <sub>2</sub> O <sub>3</sub>	
		before treatment	after treatment	before treatment	after treatment
4.88	Mn <sub>3</sub> O <sub>4</sub>	m	m	m	m
3.84	$\alpha$ -Mn <sub>2</sub> O <sub>3</sub>	m	m	—	—
3.07	Mn <sub>3</sub> O <sub>4</sub>	m	m	m	m
2.86	Mn <sub>3</sub> O <sub>4</sub>	w	w	m	w
2.76	Mn <sub>3</sub> O <sub>4</sub>	vs	s	vs	s
2.74	$\alpha$ -Mn <sub>2</sub> O <sub>3</sub>	vs	vs	—	—
2.47	Mn <sub>3</sub> O <sub>4</sub>	vs	vs	vs	vs
2.35	Mn <sub>3</sub> O <sub>4</sub>	m	m	m	w
	$\alpha$ -Mn <sub>2</sub> O <sub>3</sub>				
2.02	Mn <sub>3</sub> O <sub>4</sub>	m	w	m	w
1.98	$\alpha$ -Mn <sub>2</sub> O <sub>3</sub>	m	w	—	vw
1.84	$\alpha$ -Mn <sub>2</sub> O <sub>3</sub>	m	w	—	—
1.78	Mn <sub>3</sub> O <sub>4</sub>	m	w	—	w
Composition of the samples		MnO <sub>1.39</sub>	MnO <sub>1.40</sub>	MnO <sub>1.343</sub>	MnO <sub>1.318</sub>

markedly in the X-ray pattern of  $\alpha$ - $Mn_2O_3$  heated in  $CO_2$  stream at  $670^\circ C$  for 2 hours. With weaker intensity the reflexion of  $MnO$  can be observed in the X-ray patterns of the treated mixtures, too.

By comparing curves 15 and 16 of Fig. 5 with curves 3 and 7 it can be stated, in accordance with the results of X-ray investigations, as well as with the chemical composition that in  $N_2$  atmosphere no changes occurred in the mixtures; both the  $Mn_3O_4$  and the  $Mn_2O_3$  component remained unchanged.

## SUMMARY

Summarizing the results obtained from the IR-spectra and X-ray patterns and those of the thermal investigations, the following may be established concerning the oxidation and stability of  $Mn_3O_4$  in the temperature range of the thermal stability of the  $Mn_2O_3$ :

### A. In air

1. Though the DTA and TGA investigation of pure  $Mn_3O_4$  at the generally used heating rate ( $10^\circ C/min$ ) does not or only hardly point to oxidation, a slow oxidation of pure  $Mn_3O_4$  is proved by TGA curves taken at constant temperatures during prolonged heating (or by slow heating rate). The composition of a  $Mn_3O_4$  sample after heating at  $670^\circ C$  for 3 hours proved to be  $MnO_{1.46}$ .

2. The presence of other manganese compounds ( $MnO_2$  modifications, manganite,  $Mn_2O_3$ ) or that of  $Fe_2O_3$ , in an amount as low as 1 per cent, exerts a significant influence on the oxidation of  $Mn_3O_4$ :

a) The oxidation of  $Mn_3O_4$  is initiated and accelerated by the presence of other manganese oxides; the composition of a  $Mn_3O_4$  sample containing other manganese oxide and heated at  $660$ — $670^\circ C$  reached the value  $MnO_{1.48}$  after 1 hour, whereas the composition of a pure  $Mn_3O_4$  sample in the same conditions proved to be only  $MnO_{1.35}$ .

b) The starting temperature of the oxidation of  $Mn_3O_4$  is lowered by the presence of other manganese oxides and, depending on their quality and quantity, the oxidation starts at  $460$ — $560^\circ C$ .

c) The most intensive effect on the oxidation of  $Mn_3O_4$  is exerted by  $Mn_2O_3$ .

### B. In $CO_2$ atmosphere

1. The  $Mn_3O_4$ , also in presence of other manganese oxides, remains unchanged even after prolonged heating.

2. On the contrary, the  $Mn_2O_3$  heated in  $CO_2$  decomposes, even  $MnO$  appears as a new phase. In mixtures the  $Mn_2O_3$  shows a similar behaviour and in the IR-spectra as well as in X-ray patterns of samples heated the characteristics of  $Mn_3O_4$  are dominating beside weak traces of  $MnO$  and  $Mn_2O_3$ .

### C. In $N_2$ atmosphere

Heating in nitrogen atmosphere both  $Mn_3O_4$  and  $Mn_2O_3$  as well as their mixtures remain unchanged as it is proved by the IR-spectra and X-ray patterns.

Thus, in the temperature range of the thermal stability of the  $Mn_2O_3$ :

a) if a possibility of oxidation exists, the  $Mn_3O_4$  will be oxidized into  $Mn_2O_3$ , slower or faster;

b) if the possibility of oxidation is excluded, both the  $Mn_3O_4$  and  $Mn_2O_3$  remain unchanged, and

c) if the thermal effect is associated with  $CO_2$  atmosphere, the  $Mn_3O_4$  remains unchanged, the  $Mn_2O_3$  will be, however, transformed into  $Mn_3O_4$ , and even,  $MnO$  appears as a new phase.

It seems that the experimental facts summarized above may be used in interpreting the formation of manganese oxide assemblages in different metamorphic processes.

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