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AN EXPERIMENTAL STUDY OF SiO₂ SOLUBILITY IN HAUSMANNITE

by

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(with 3 text-figures and 3 tables)

Abstract

Solid solubility of SiO₂ component in hausmannite has been experimentally determined. The solid solubility of hausmannite coexisting with rhodonite in air at 1200°C determined by microprobe analyses is the atomic ratio Si/(Mn+Si) of 0.015(2). Reaction between hausmannite and quartz at 900°C under hematite-magnetite buffer was not attained in equilibrium. Metastable Mn₃O₄-SiO₂ solid solutions have been synthesized in air at 60°C by a coprecipitation method. The atomic ratio Si/(Mn+Si) is achieved to about 0.025 by this way. It is indicated that the increase of Si content in hausmannite decreases the lattice parameter *c* and increases *a* slightly. Concentrations of constituent ions and cation vacancy in hausmannite have been calculated as a function of Po₂ and temperature by using a defect chemical equilibrium relations. Possibility to finding the natural hausmannite which is supersaturated with SiO₂ is suggested.

Introduction

Hausmannite Mn₃O₄ is found in low-grade metamorphosed manganese ores. Although such a hausmannite is associated with braunite, Mn-pyroxens and quartz (e. g. Roy, 1981), the most hausmannite has nearly the ideal composition and contains only a little silica. According to the phase diagram of Mn₃O₄-SiO₂ studied by Muan (1959a, 1959b), no solid solubility is found along the join even over 1000°C in air and at various levels of oxygen partial pressures. It is well known that the substitution of cation in M²⁺M³⁺₂O₄-type cubic spinel by tetra-valent cation (such as Si, Ti) causes metal vacancy in the structure. Since the hausmannite has a tetragonally distorted spinel structure, it may be possible to form a solid solution with SiO₂ by the same manner, even if its amount is small.

Precise measurement of the change of lattice parameters is an useful technique to determine the limit of solid-solubility and to estimate the valence state of constituent ions. A defect thermodynamic calculation together with the above technique was successful for estimation of the valence state of cations and vacancies in the system SnO₂-Sb₂O₄ system (Kikuchi & Umehara, 1985). The equilibrium concentrations of cations and cation vacancy of the solid solutions in the system Mn₃O₄-MnFe₂O₄ were estimated by the same manner (Osawa et. al. 1992). They showed that the lattice parameters of the solid solution at a certain metal ratio

Mn/Fe are changeable with temperature and P_{O_2} .

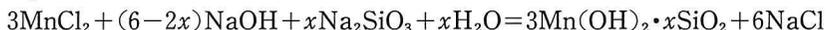
In some cases, coprecipitation with a successive heat treatment at a suitable temperature causes a metastable formation of solid solution, of which chemical composition is beyond the solubility limit. Catalysts in the system $SnO_2-Sb_2O_4$ have been prepared by a such method (Herrmann et al. 1979). We aimed also to synthesize metastable hausmannite solid solutions which are supersaturated by silica. This may be relevant to the formation process of hausmannite under low-grade metamorphism.

Experimental procedure

Hausmannite as a starting material was synthesized from a reagent grade MnO_2 at $1100^\circ C$ for 3 hours in air. A mixture, hausmannite+quartz in 4:1 molar ratio, was then prepared by mixing the hausmannite and a reagent grade SiO_2 (quartz). The mixture was ground in alcohol and dried. Starting materials for the experiments in air and under $Fe_3O_4-Fe_2O_3$ buffer were the same.

Experimental procedure under $Fe_3O_4-Fe_2O_3$ buffer were as follows. The $Fe_3O_4-Fe_2O_3$ buffer was put at the lower part of a silica tube and a small amount of silica-glass wool was stuffed. Then hausmannite or the mixture was put at the upper part of the tube and vacuum-sealed. The tube was heated at $900^\circ C$ for 6 days.

Metastable hausmannite solid solutions were synthesized from coprecipitates as follows. Reagent grade $MnCl_2 \cdot 4H_2O$ and Na_2SiO_3 were measured off to the several Mn:Si ratios and dissolved in water separately. The sodium hydroxide solution was added to the Na_2SiO_3 solution. Then the two solutions were mixed. The silica content in coprecipitate was adjusted according to the x of the following equation,



The coprecipitates were washed with distilled water and dried at $60^\circ C$ in air for 3 days. The solid solutions of hausmannite with SiO_2 were formed during the successive oxydation and dehydration. The exact compositions of coprecipitate were not determined.

Microprobe analysis of the synthesized hausmannite solid solution (grains about $5-10 \mu m$ in diameter) was made using a JEOL JCMA-733, at 15 kV operating voltage and $2 \mu m$ beam diameter. ZAF corrections were made based on the formula Mn_3O_4 using the reduction program of Yui (1992).

Identification of run product was made by X-ray powder diffraction technique with an diffractometer using graphite monochromated $CuK\alpha$ radiation. Lattice parameters of hausmannite and hausmannite solid solution were determined with scanning speed $1/4^\circ \text{min}^{-1}$. Silicon powder was used as an internal standard. The parameters were refined by the least-squares method.

Experimental results

Syntheses in air at high temperatures and by Fe₃O₄–Fe₂O₃ buffer

Experimental data are given in Table 1. A mineral assemblage, braunite +

Table 1 Experimental result of runs in air and under buffer condition.

run No.	HA	1A	2A	HB	1B
starting material	Mn ₃ O ₄	4Mn ₃ O ₄ +SiO ₂	4Mn ₃ O ₄ +SiO ₂	Mn ₃ O ₄	4Mn ₃ O ₄ +SiO ₂
temperature (°C)	1200	1100	1200	940	900
duration (days)	6	8	6	6	6
condition	air	air	air	buffer	buffer
associated phase	—	braunite	rhodonite	—	quartz

hausmannite was obtained from the mixture at 1100°C and an assemblage, hausmannite and rhodonite at 1200°C. These results agreed well with those by Abs-Wurmbach et al. (1983). The pure hausmannite transforms to a cubic spinel structure at 1160°C and this transformation is unquenchable (Van Hook and Keith, 1958). The hausmannite solid solution formed at 1200°C appeared to be polysynthetic twins. Microprobe analysis (average of 11) gave Mn₃O₄ 99.8(5), SiO₂ 0.44(6), sum 100.3(5)wt%, yielding an atomic ratio Si/(Mn+Si)=0.015(2). It is however impossible to show the chemical formula due to the lack of analysis data for oxygen. The value indicates that the solubility limit at lower temperatures will be a negligibly small. The lattice parameters refined are listed in Table 2. It is indicated that the value of parameter *c* decreases clearly with the addition of SiO₂ and *a* increases slightly.

The mineral assemblage obtained after the run at 900°C under Fe₃O₄–Fe₂O₃ buffer condition were hausmannite and quartz. It is indicated that the equilibrium between the quartz and the hausmannite is not attained. Lattice parameters of the hausmannite are almost the same with those of pure Mn₃O₄ obtained under the same condition (Table 2).

Table 2 Lattice parameters of hausmannite–SiO₂ solid solution and hausmannites listed in Table 1.

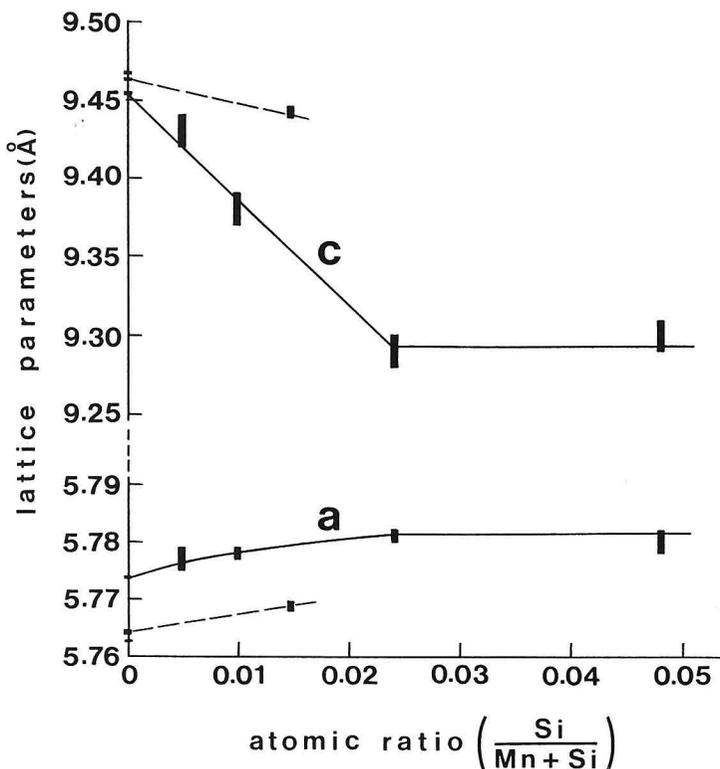
run No.	ratio Si/(Mn+Si)	temperature (°C)	condition	lattice parameters	
				a (Å)	c (Å)
2A	0.015(2)	1200	air	5.7688(8)	9.442(3)
HA	0.00	1200	air	5.7643(4)	9.4626(7)
HB	0.00	940	buffer	5.7630(1)	9.467(1)
1B	n. d.	900	buffer	5.763(1)	9.471(2)

Syntheses by coprecipitation

Compositions and lattice parameters of hausmannite solid solution are listed in Table 3. The relationship between cell parameters and silica content are shown in

Table 3 Starting compositions and the lattice parameters of hausmannite-SiO₂ solid solution synthesized by coprecipitation method.

run No.	ratio Si/(Mn+Si)	lattice parameters	
		a (Å)	c (Å)
Pr1	0.0	5.7739(2)	9.4543(8)
Pr2	0.005	5.777(2)	9.43(1)
Pr3	0.010	5.778(1)	9.38(1)
Pr4	0.024	5.781(1)	9.29(1)
Pr5	0.048	5.780(2)	9.30(1)
Pr6	0.200	amorphous phase	

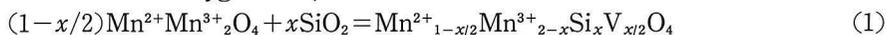


Text-fig. 1 Plots of lattice parameters as a function of the ratio Si/(Mn+Si). Solid lines are for the samples by coprecipitation method and dashed lines are for the samples by heating in air at 1200°C.

Text-fig. 1. It is shown that the parameter *a* slightly increases whereas the parameter *c* remarkably decreases, with increasing silica content up to the ratio Si/(Mn+Si)=0.025. The both parameters then remains at constant above this value. It is indicated that the solubility limit by this method is about the ratio 0.025. Two phases, hausmannite solid solution and an amorphous substance, are coexisted above this ratio.

Discussion

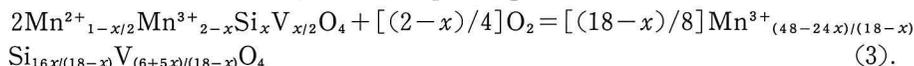
The formation of Mn₃O₄–SiO₂ solid solution can be expressed by a fundamental reaction for four oxygen ions,



where V denotes cation vacancy in the structure. The above reaction indicates that the addition of SiO₂ component decreases the numbers of Mn³⁺ and Mn²⁺ ions and creates cation vacancies. However, these concentrations is simultaneously also related to oxygen partial pressure Po₂ as shown by an oxidation reaction for pure hausmannite,



For Mn₃O₄–SiO₂ solid solution, the corresponding reaction will be written as



Applying a defect thermodynamic approach which has been used similarly for the system Mn₃O₄–MnFe₂O₄ (Osawa et. al., 1992), the elemental equilibrium reaction for eqn. (3) can be expressed with



We should expect an equilibrium to be attained which satisfy the condition

$$[\text{Mn}^{3+}]^2[\text{O}^{2-}][\text{V}]^{3/4} = k\text{Po}_2^{1/2}[\text{Mn}^{2+}]^2 \quad (5)$$

where *k* is the equilibrium constant at the temperature. The following relations among the ionic fractions of the above chemical species are holded.

$$[\text{Mn}^{2+}] + [\text{Mn}^{3+}] + [\text{Si}^{4+}] + [\text{V}] + [\text{O}^{2-}] = 1 \quad (6)$$

where [O²⁻] is constant at 4/7 due to the formula.

For a given ratio of Si to Mn ($\equiv \alpha$),

$$[\text{Si}^{4+}] = \alpha \{ [\text{Mn}^{2+}] + [\text{Mn}^{3+}] \} \quad (7)$$

where α is equal to $2x/(6-3x)$ in eqn. (3). For charge balance,

$$2[\text{O}^{2-}] = 2[\text{Mn}^{2+}] + 3[\text{Mn}^{3+}] + 4[\text{Si}^{4+}] \quad (8).$$

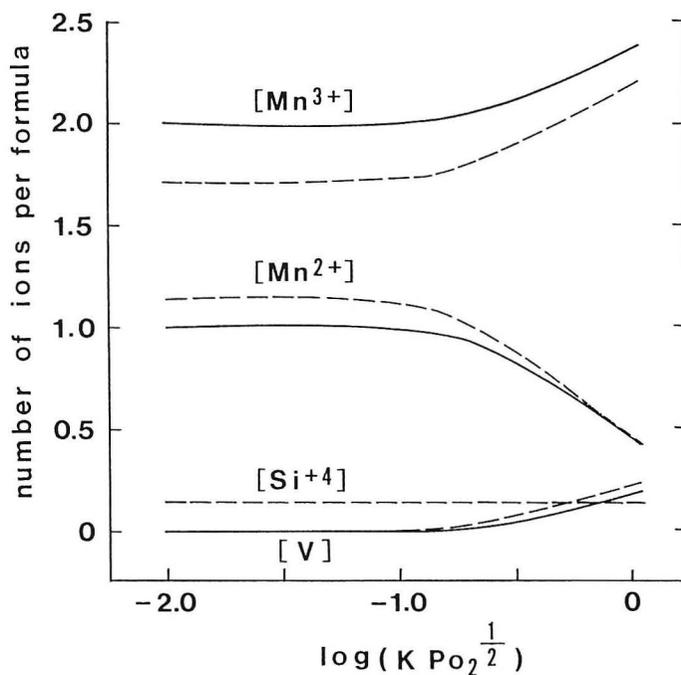
From eqns. (6)~(8) we obtain

$$[\text{Mn}^{2+}] = \frac{4}{7+14\alpha} - \frac{3+4\alpha}{2+4\alpha}[\text{Mn}^{3+}] \quad (9),$$

$$[\text{V}] = \frac{3}{7} - \frac{4+4\alpha}{7+14\alpha} + \frac{1+\alpha}{2+4\alpha}[\text{Mn}^{3+}] \quad (10),$$

$$[\text{Si}^{4+}] = \frac{4\alpha}{7+14\alpha} - \frac{\alpha}{2+4\alpha}[\text{Mn}^{3+}] \quad (11).$$

Substituting of eqns. (9)~(11) in eqn. (5), [Mn³⁺] is expressed in terms of equilibrium constant *k*, Po₂, and α . By giving a numerical value to the product $k\text{Po}_2^{1/2}$, one can calculate [Mn³⁺] for a given α . Subsequently, the other concentrations are calculated by eqns. (9)~(11). The number of each cation and that of vacancy in Mn₃O₄–SiO₂ solid solution as a function of $k\text{Po}_2^{1/2}$ for $\alpha=0$ and for $\alpha=0.05$ ($x=0.14$) are shown in Text—fig. 2. The figure demonstrates the following features.



Text-fig. 2 Number of cations and cation vacancy per formula as a function of $\log(k\text{Po}_2^{1/2})$. Solid lines are for pure Mn_3O_4 and dashed lines are for hausmannite solid solution of 0.05 of the ratio $\text{Si}/(\text{Mn}+\text{Si})$.

(i) Under low Po_2 and at low temperatures ($k\text{Po}_2^{1/2} < 10^{-1.5}$)

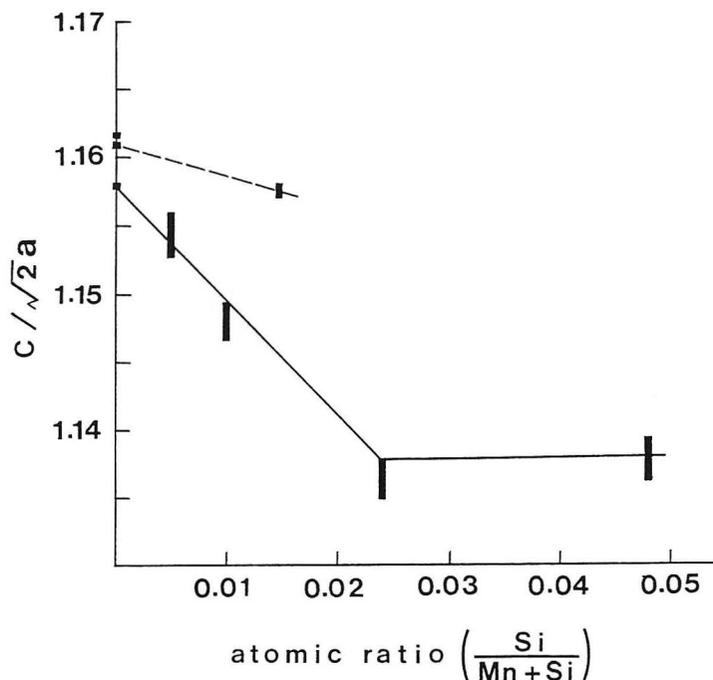
Cation vacancies are nothing and $[\text{Mn}^{2+}]$ exceeds 1. This indicates some Mn^{2+} ions must occupy the octahedral sites in the structure. The excess Mn^{2+} and the excess Si make the component $\text{Mn}^{2+}[\text{Mn}^{2+}\text{Si}]\text{O}_4$ of which formula is just the same as tephroite. Abs-Wurmbach et. al. (1983) found the stable assemblage of tephroite and hausmannite under $\text{Po}_2 < 10^{-10}$ at 600°C and at total pressure 4 kb. Actually, SiO_2 may be therefore less soluble in this case.

(ii) Under relatively high Po_2 and at high temperatures ($k\text{Po}_2^{1/2} > 10^{-1.5}$)

The number of Mn^{3+} increases with increasing Po_2 and decreases with increasing SiO_2 content.

All the present experimental results except one obtained by hematite-magnetite buffer should be explained by the case (ii). The reaction between SiO_2 and Mn_3O_4 is not occurred at the 900°C by hematite-magnetite buffer. But the starting Mn_3O_4 is thought to be reached at equilibrium with Po_2 because the a and c parameters agreed well with those of Mn_3O_4 studied under the same condition. The Mn_3O_4 thus obtained should be nearly stoichiometric because the product $k\text{Po}_2$ has been small.

The deviation from the cubic symmetry of the tetragonal spinel $\text{Mn}^{2+}\text{Mn}^{3+}_2\text{O}_4$



Text-fig. 3 Dependence of distortion ratio $c\sqrt{2}a$ against the ratio $\text{Si}/(\text{Mn}+\text{Si})$. Solid lines are for the samples by coprecipitation method and dashed lines are for the samples by heating in air at 1200°C.

has been explained by a cooperative phenomenon of Jahn Teller effect of the distorted Mn^{3+}O_6 octahedra in its structure (Kanamori, 1960). It is therefore expected that the decrease of Mn^{3+} in the structure decreases the parameter c of which direction corresponds to one of $\text{O}^{2-}-\text{Mn}^{3+}-\text{O}^{2-}$ direction of Mn^{3+}O_6 octahedra. It is indicated by the structural relation of hausmannite to the cubic spinel that the axis of the pseudo-cubic cell is related to $\sqrt{2}a$. The distortion ratio of hausmannite is therefore expressed by $c/\sqrt{2}a$. The dependence of the distortion ratio to the ratio $\text{Si}/(\text{Mn}+\text{Si})$ is shown in Text-fig. 3. The solid line is by the coprecipitation method and the dashed line by the experiment in air. The difference between two lines will be due to the difference of oxidation state.

We have inferred that hausmannites altered at low temperatures after braunite or other Mn-minerals may have contained a considerable amount of SiO_2 at the initial stage.

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