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THE STABILITY AND PHASE TRANSITION OF THE SYSTEM $\text{Fe}_2\text{GeO}_4\text{-Fe}_2\text{SiO}_4$

by

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(with 3 Text-Figures)

(Contribution from the Department of Geology and Mineralogy, Faculty of
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Abstract

The stability of Fe_2GeO_4 as a function of oxygen fugacity (f_{O_2}) has been studied hydrothermally by means of the oxygen buffer technique. At 800°C , Fe_2GeO_4 is stable from f_{O_2} defined by wüstite-magnetite buffer up to f_{O_2} defined by magnetite-hematite buffer. Within its stability field, Mössbauer spectra indicated that only ferrous ions were present in the iron-germanate spinel under investigation. At the oxygen fugacity defined by iron-wüstite, Fe_2GeO_4 is reduced to Fe-Ge alloy. Within the oxygen fugacities defined by wüstite-magnetite and fayalite-quartz-magnetite buffers, both Fe_2GeO_4 and Fe_2SiO_4 are stable and $\text{Fe}_2(\text{Ge}_x\text{Si}_{1-x})\text{O}_4$ solid solutions of any proportions of Ge and Si are present.

The olivine-spinel transition of the system $\text{Fe}_2\text{GeO}_4\text{-Fe}_2\text{SiO}_4$ has been studied within the stability field of both Fe_2GeO_4 and Fe_2SiO_4 by hydrothermal and by high pressure piston-cylinder techniques. An isothermal (800°C) px phase diagram was determined up to pressure of 40 kilobars. Complete solid solution in the spinel phase were observed up to 50 mole percent of Fe_2SiO_4 in this system. Extrapolation of the spinel phase boundary to pure fayalite indicates that the pressure of olivine-spinel transition for Fe_2SiO_4 is 50 Kb at this temperature.

Introduction

The olivine-spinel transition of the system $\text{Fe}_2\text{GeO}_4\text{-Fe}_2\text{SiO}_4$ has been investigated previously by RINGWOOD (1958) at 700°C and 25 kilobars. Because of the various possible oxidation states of iron and germanium, the control of the oxidation state of Fe^{+2} and Ge^{+4} must be considered. In the previous experiment of Ringwood, slight excess of metallic iron was introduced into the system presumably

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to control the oxidation state of iron. However, it was suspected that spinel of the form $\text{Fe}_2^{+3}\text{Ge}^{+2}\text{O}_4$ might be formed due to the reaction $2\text{Fe}^{+2} + \text{Ge}^{+4} = 2\text{Fe}^{+3} + \text{Ge}^{+2}$ (RINGWOOD, 1958).

Thermodynamic data indicate that the free energy of reaction for the equation $2\text{Fe} + \text{GeO}_2 = 2\text{FeO} + \text{Ge}$ is negative by about 8 Kcal/mole 700°C (MAH and ADAMI, 1963; WAI et al., 1968). Thus, at the oxygen fugacity of iron-wüstite, GeO_2 will be reduced to Ge metal and combined with iron to form iron-germanium alloy. The stability of Fe_2GeO_4 at oxygen fugacities defined by iron-wüstite is thus doubtful.

We have recently synthesized Fe_2GeO_4 hydrothermally and investigated its stability at various oxygen fugacities by means of the oxygen buffer technique of EUGSTER (1957). Mössbauer spectra of iron-germanate, synthesized at various oxygen fugacities, were studied to identify the oxidation state of iron. The olivine-spinel transition in the system $\text{Fe}_2\text{GeO}_4\text{-Fe}_2\text{SiO}_4$ was then investigated within its stability field by hydrothermal and piston-cylinder high pressure techniques.

Experimental

Conventional hydrothermal apparatus was used for pressures lower than 2 kilobars with oxygen fugacities controlled by the oxygen buffer technique (EUGSTER, 1957; ERNST, 1960, 1962; EUGSTER and WONES, 1962). High pressure experiments above 7 kilobars were carried out in a single stage piston-cylinder apparatus (BOYD and ENGLAND, 1960; KENNEDY and LAMORI, 1962; NEWTON and KENNEDY, 1963). The working volume was of 1/2" diameter and 2" length with talc served as the pressure transmitting medium. Reported pressures are believed to be correct to within 1 kilobar. Temperature was measured by a chromel-alumel thermocouple placed in a hole in the furnace assembly. Temperature fluctuations were within a few degrees.

Dehydrated germanium dioxide (Johnson Matthey & Co. Ltd.), reagent grade silicic acid (Baker Chemical Co.), dehydrated to cristobalite, and iron powder (99% pure, Baker Chemical Co.) were used starting materials.

Post-run phase identifications were made by x-ray diffraction and polarizing microscope.

Results

(1). The stability of Fe_2GeO_4 and Fe_2SiO_4 as a function of oxygen fugacity.

The stability of Fe_2GeO_4 spinel as a function of f_{O_2} was studied employing oxygen buffers. Charges for the synthesis of Fe_2GeO_4 by hydrothermal technique were prepared using finely ground powders of $2\text{Fe} + \text{GeO}_2$ or $\text{Fe}_2\text{O}_3 + \text{GeO}_2$ mixtures in the stoichiometric proportions of Fe_2GeO_4 . Excess H_2O was sealed with the

Table 1. The stability of Fe_2GeO_4 at various values of f_{O_2} .

Sample charge	P_{fluid}	Temp. ($^{\circ}\text{C}$)	O_2 -buffer	Result
Fe_2GeO_4	500 b	800	I Q F	Fe-Ge alloy
$2\text{Fe} + \text{GeO}_2$	1000 b	800	I W	Fe-Ge alloy
Fe_2GeO_4	500 b	900	I W	Fe-Ge alloy
$2\text{Fe} + \text{GeO}_2$	500 b	800	WM	Fe_2GeO_4
$2\text{Fe} + \text{GeO}_2$	500 b	900	WM	Fe_2GeO_4
$\text{Fe}_2\text{O}_3 + \text{GeO}_2$	500 b	800	F Q M	Fe_2GeO_4
$2\text{Fe} + \text{GeO}_2$	1000 b	800	Ni-NiO	Fe_2GeO_4
$\text{Fe}_2\text{O}_3 + \text{GeO}_4$	500 b	800	HM	Fe_2GeO_4
Fe_2GeO_4	atmosphere	900	in air	$\text{Fe}_2\text{O}_3 + \text{GeO}_2$

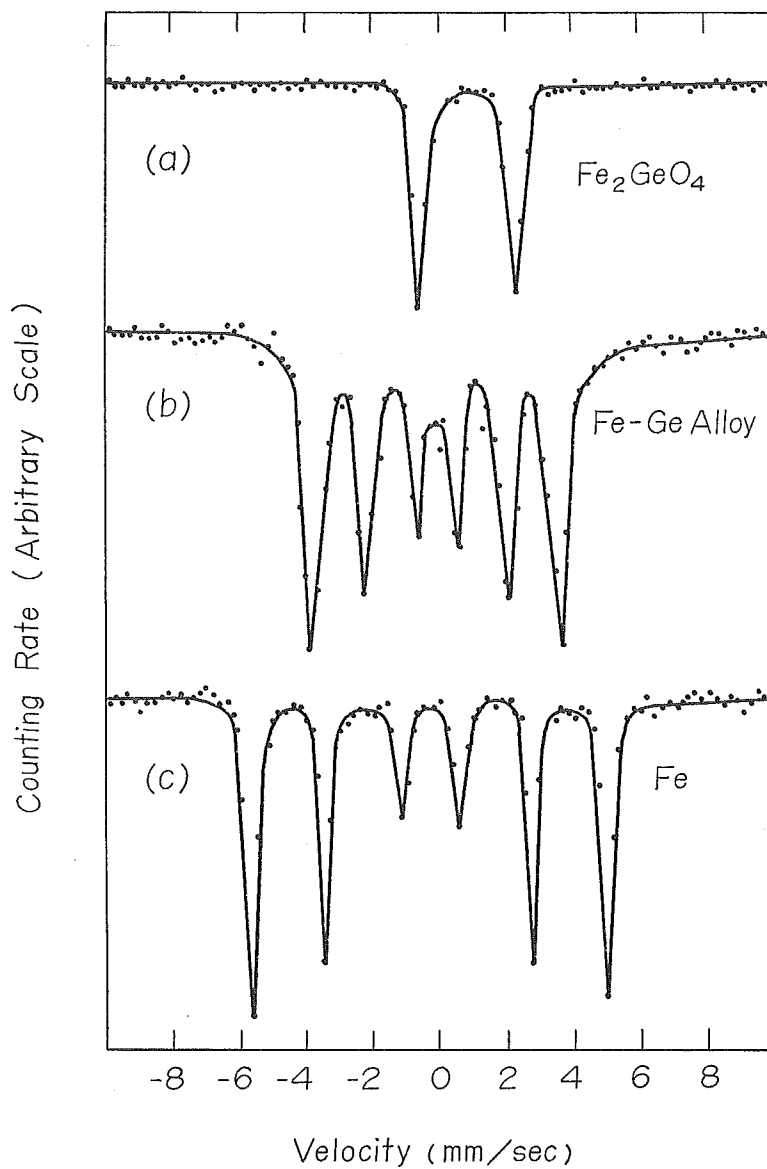
IQF : iron-quartz-fayalite ; IW : iron-wüstite ; WM : wüstite-magnetite ; FQM : fayalite-quartz-magnetite ; HM : hematite-magnetite.

powder in a silver capsule and the sample charge so prepared was then treated hydrothermally at 800°C and 500 bars for 2 to 3 days. The synthesized homogeneous phase consisted of transparent greenish-brown crystals. The unit cell edge of the synthesized Fe_2GeO_4 spinel was determined by x-ray diffractometer techniques with a scanning speed of $1/4$ degree per minute using sodium chloride as an internal standard. In all cases the (311) and (220) peaks of the spinel were used for lattice parameter measurements. The unit cell edge of Fe_2GeO_4 spinel synthesized in this work and values reported by other investigators are given in Table 2.

Table 2. Lattice parameter of Fe_2GeO_4 spinel.

This work	Rossiter (1966)	Durif-Varambon et al. (1956)	Ringwood (1958)
$8.414 \pm 0.002 \text{ \AA}$	8.413 \AA	8.411 \AA	8.401 \AA

The Mössbauer spectrum of the synthesized Fe_2GeO_4 spinel (Fig. 1a) indicates that only ferrous ions in octahedral site were present in the synthetic material. The isomer shift and quadrupole splitting derived from the spectrum are $1.0 \pm 0.1 \text{ mm sec}^{-1}$ and $2.8 \pm 0.1 \text{ mm sec}^{-1}$ respectively, which are in good agreement with the Mössbauer parameters of Fe_2GeO_4 reported in the literature (Rossiter, 1966; Mathur et al., 1965). At the oxygen fugacity defined by iron-wüstite buffer, Fe_2GeO_4 decomposed to form an opaque, gray-black and ferro-magnetic substance. The x-ray diffraction pattern of the magnetic substance became definite after several cycles of grinding and re-heating at the same temperature and oxygen fugacity. The observed crystal structure was hexagonal with $a=5.18 \text{ \AA}$ and $c=4.23 \text{ \AA}$. This is similar to Fe_3Ge reported by SHOTL'GTS and GEL'D (1962). Some Ge was presumably lost to the capsule wall during the re-heating processes. The Mössbauer spectrum of this magnetic substance is shown in Fig. 1b. Mössbauer parameters derived from the spectrum I.S. = 0.3 mm sec^{-1} and $H=238 \text{ KOe}$ are close to those

**Fig. 1.**

Mössbauer absorption spectra (source: Co^{57} in Pd). (a). Fe_2GeO_4 at f_{O_2} defined by FQM buffer. (b). Fe_2GeO_4 at f_{O_2} defined by IW buffer. (c). Metallic iron.

reported for Fe_3Ge alloy (YAMAMOTO, 1965). For comparison the Mössbauer spectrum of Fe is given in Fig. 1c. When Fe_2GeO_4 spinel was heated under atmospheric conditions at 900°C , it decomposed to Fe_2O_3 and GeO_2 .

The stability field of Fe_2SiO_4 (olivine) is limited to the f_{O_2} , defined by the IQF (iron-quartz-fayalite) equilibrium boundary and FQM (fayalite-quartz-magnetite) equilibrium boundary. (EUGSTER and WONES, 1962, ERNST, 1962). Within the f_{O_2} , defined by WM (wüstite-magnetite) and FQM buffers, both Fe_2GeO_4 and Fe_2SiO_4 are stable and $\text{Fe}_2(\text{Ge}_x\text{Si}_{1-x})\text{O}_4$ solid solutions in any proportions of Ge and Si are present.

(2). Olivine-spinel transition in the system $\text{Fe}_2\text{GeO}_4\text{-Fe}_2\text{SiO}_4$.

Mixtures of finely powdered iron and $\text{SiO}_2\text{+GeO}_2$ in the stoichiometric proportions of $\text{Fe}_2(\text{Ge}_x\text{Si}_{1-x})\text{O}_4$ solid solutions were prepared for sample charges. Low pressure experiments (below 2 kilobars) were carried out by hydrothermal technique with oxygen fugacities controlled by FQM buffer. High pressure runs were performed with a piston-cylinder apparatus without control of f_{O_2} . No

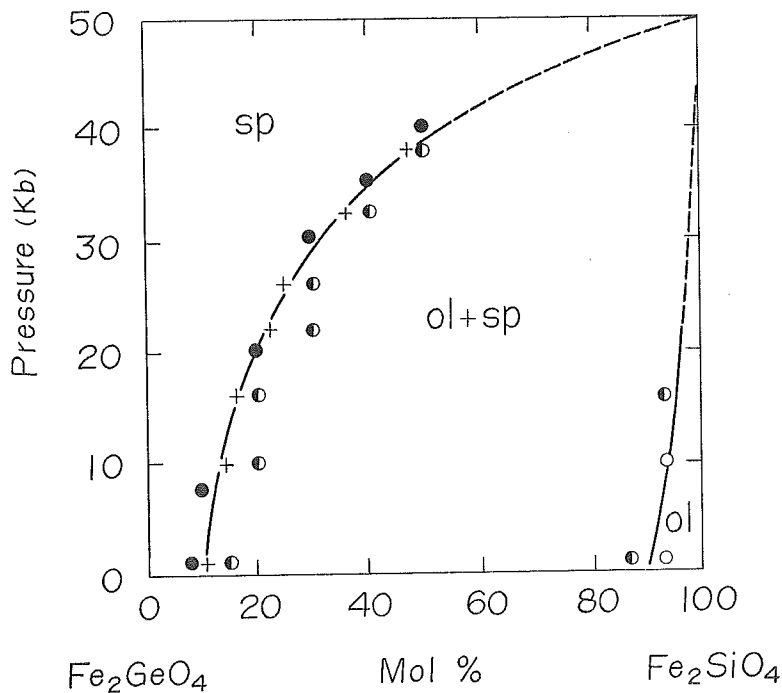


Fig. 2.

Isothermal section of the system $\text{Fe}_2\text{GeO}_4\text{-Fe}_2\text{SiO}_4$ at 800°C .

- olivine phase ;
- spinel phase ;
- ⊙ olivine+spinel phases ;
- + composition of spinel (ss) in co-existing two phases.

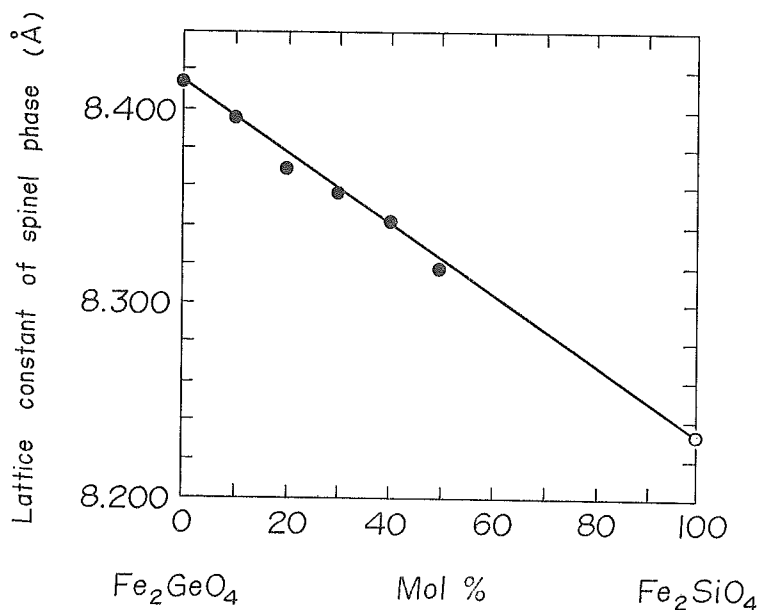


Fig. 3. Change of lattice constant with composition of the Fe_2GeO_4 - Fe_2SiO_4 spinel solid solution. (The value of Fe_2SiO_4 spinel is after Akimoto and Fujisawa, 1965).

excess metallic iron was introduced in the high pressure runs for reasons to be discussed later. A drop of water was added to the sample charge for high pressure experiments to promote the reaction. The duration of each run was usually 2 to 3 days.

The isothermal phase relationships at 800°C in the system Fe_2GeO_4 - Fe_2SiO_4 were determined up to 40 kb as shown in Figure 2. The lattice parameters of the spinel solid solution were determined in the similar way to the case of Fe_2GeO_4 . They are plotted as a function of the mole fraction of Si in the spinel phase of the Fe_2GeO_4 - Fe_2SiO_4 system in Figure 3. All points fall virtually on a straight line connecting the unit cell edge of Fe_2GeO_4 spinel determined in this work and the corresponding value for Fe_2SiO_4 spinel ($8.234 \pm 0.001 \text{Å}$) determined by RINGWOOD (1958) and AKIMOTO (1965). Vegard's law appears to be valid for this binary solid solution series.

Discussion

Unlike Mg_2GeO_4 , which converts from the spinel form into the olivine form above 810°C and at atmospheric pressure (DACHILLE and ROY, 1961), Fe_2GeO_4 synthesized hydrothermally at 900°C and 500 bars in this experiment is a normal

spinel. The spinel form of Fe_2GeO_4 has been reported to exist at $1,000^\circ\text{C}$ in vacuum (MATHUR et al., 1965). Mössbauer spectra of the synthesized Fe_2GeO_4 indicate that within its stability range (from f_{O_2} defined by wüstite-magnetite buffer up to f_{O_2} defined by magnetite-hematite buffer at 800°C), only ferrous ions were present in the octahedral site of the iron-germanate spinel. The fact that ferric ions were not observed in the Mössbauer spectra indicates that $\text{Fe}_2^{+3}\text{Ge}^{+2}\text{O}_4$ probably does not exist under the investigated conditions.

CHURBAKOV et al., (1963) have reported the synthesis of magnetite containing bivalent germanium in the form $(\text{Fe}_{1-x}\text{Ge}_x)\text{O}\cdot\text{Fe}_2\text{O}_3$ with $x=0.25, 0.50$ and 0.75 . Thus, if excess iron is present in the system and is oxidized to Fe_3O_4 , then magnetite solid solutions with bivalent germanium replacing ferrous iron may be possible. On the other hand, if the excess iron in the system is present in the metallic form, the formation of Fe-Ge alloy will take place. The disadvantages of having excess of iron are thus obvious.

In the hydrothermal system, the oxygen fugacity of the sample charge can be well defined by using oxygen buffer technique as shown Table 1. At f_{O_2} defined by fayalite-quartz-magnetite buffer, both Fe_2GeO_4 and Fe_2SiO_4 are stable and the binary system $\text{Fe}_2\text{GeO}_4\text{-Fe}_2\text{SiO}_4$ of any proportions of Ge and Si can be studied. However, the control of the oxygen fugacity in the high pressure piston-cylinder apparatus is difficult.

Olivine-spinel transition of the system $\text{Fe}_2\text{GeO}_4\text{-Fe}_2\text{SiO}_4$ has been used to evaluate the transition pressure of fayalite from the olivine form to the spinel form. RINGWOOD (1957) has derived thermodynamic equations to calculate the pressure of olivine-spinel phase transition for orthosilicates from the germanate-silicate solid solution by assuming ideal solution behavior. Based on his experimental data of the coexisting olivine and spinel phases in the system $\text{Fe}_2\text{GeO}_4\text{-Fe}_2\text{SiO}_4$ at 700°C and 25 kilobars (spinel: $\text{Fe}_2(\text{Ge}_{0.75}\text{Si}_{0.25})\text{O}_4$; olivine: $\text{Fe}_2(\text{Ge}_{0.05}\text{Si}_{0.95})\text{O}_4$), RINGWOOD (1958) calculated the olivine-spinel transition of fayalite should take place at 50 kilobars at 700°C .

Recently, AKIMOTO and FUJISAWA (1965) has experimentally determined the pressure of olivine-spinel transition in fayalite. They obtained an empirical equation relating to the transition pressure and temperature as $P=12.0+0.45T$, where P is in kilobars and T in degrees centigrade. According to their empirical equation, the olivine-spinel transition of fayalite should take place at 43.5 kilobars at 700°C .

Complete solid solutions in the spinel phase of the $\text{Fe}_2\text{GeO}_4\text{-Fe}_2\text{SiO}_4$ system up to 50 mol per cent of Fe_2SiO_4 were observed in this work up to the pressure of 40 kilobars at 800°C . Extrapolation of the spinel phase boundary of the $\text{Fe}_2\text{GeO}_4\text{-Fe}_2\text{SiO}_4$ system to that of pure Fe_2SiO_4 is shown in Figure 3 to be around 50 kilobars. The extrapolated value obtained from this experiment is very close to AKIMOTO and FUJISAWA's determination of 48 kilobars at 800°C for the olivine-spinel transition of fayalite.

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