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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)

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## *Abstract*

The stability of  $\text{Fe}_2\text{GeO}_4$  as a function of oxygen fugacity ( $f_{\text{O}_2}$ ) has been studied hydrothermally by means of the oxygen buffer technique. At  $800^\circ\text{C}$ ,  $\text{Fe}_2\text{GeO}_4$  is stable from  $f_{\text{O}_2}$  defined by wüstite-magnetite buffer up to  $f_{\text{O}_2}$  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,  $\text{Fe}_2\text{GeO}_4$  is reduced to Fe-Ge alloy. Within the oxygen fugacities defined by wüstite-magnetite and fayalite-quartz-magnetite buffers, both  $\text{Fe}_2\text{GeO}_4$  and  $\text{Fe}_2\text{SiO}_4$  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  $\text{Fe}_2\text{GeO}_4$  and  $\text{Fe}_2\text{SiO}_4$  by hydrothermal and by high pressure piston-cylinder techniques. An isothermal ( $800^\circ\text{C}$ ) 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  $\text{Fe}_2\text{SiO}_4$  in this system. Extrapolation of the spinel phase boundary to pure fayalite indicates that the pressure of olivine-spinel transition for  $\text{Fe}_2\text{SiO}_4$  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  $700^\circ\text{C}$  and 25 kilobars. Because of the various possible oxidation states of iron and germanium, the control of the oxidation state of  $\text{Fe}^{+2}$  and  $\text{Ge}^{+4}$  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  $700^\circ\text{C}$  (MAH and ADAMI, 1963; WAI et al., 1968). Thus, at the oxygen fugacity of iron-wüstite,  $\text{GeO}_2$  will be reduced to Ge metal and combined with iron to form iron-germanium alloy. The stability of  $\text{Fe}_2\text{GeO}_4$  at oxygen fugacities defined by iron-wüstite is thus doubtful.

We have recently synthesized  $\text{Fe}_2\text{GeO}_4$  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  $\text{Fe}_2\text{GeO}_4$  and  $\text{Fe}_2\text{SiO}_4$  as a function of oxygen fugacity.

The stability of  $\text{Fe}_2\text{GeO}_4$  spinel as a function of  $f_{\text{O}_2}$  was studied employing oxygen buffers. Charges for the synthesis of  $\text{Fe}_2\text{GeO}_4$  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  $\text{Fe}_2\text{GeO}_4$ . Excess  $\text{H}_2\text{O}$  was sealed with the

Table 1. The stability of  $\text{Fe}_2\text{GeO}_4$  at various values of  $f_{\text{O}_2}$ .

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

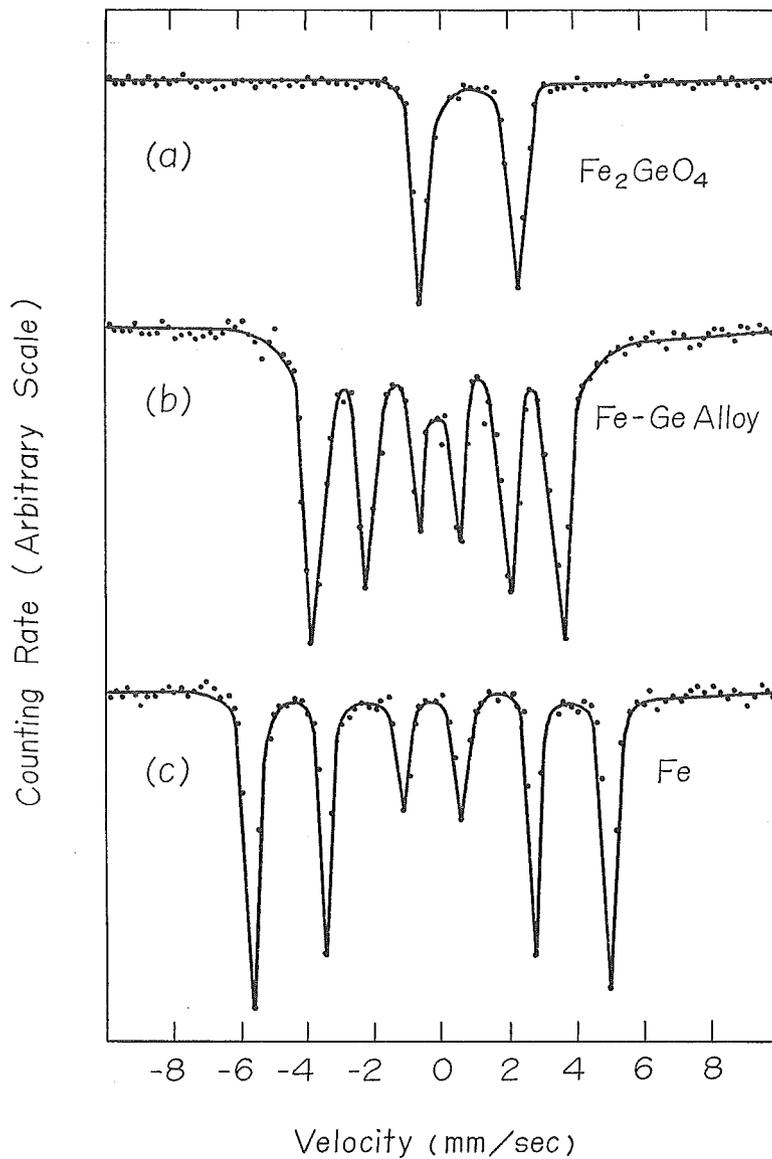
IQF : iron-quartz-fayalite ; IW : iron-wüstite ; WM : wüstite-magnetite ; FQM : fayalite-quartz-magnetite ; HM : hematite-magnetite.

powder in a silver capsule and the sample charge so prepared was then treated hydrothermally at  $800^{\circ}\text{C}$  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  $\text{Fe}_2\text{GeO}_4$  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  $\text{Fe}_2\text{GeO}_4$  spinel synthesized in this work and values reported by other investigators are given in Table 2.

Table 2. Lattice parameter of  $\text{Fe}_2\text{GeO}_4$  spinel.

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

The Mössbauer spectrum of the synthesized  $\text{Fe}_2\text{GeO}_4$  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  $\text{Fe}_2\text{GeO}_4$  reported in the literature (Rossiter, 1966; Mathur et al., 1965). At the oxygen fugacity defined by iron-wüstite buffer,  $\text{Fe}_2\text{GeO}_4$  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  $\text{Fe}_3\text{Ge}$  reported by SHOTL'ITS 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. =  $0.3 \text{ mm sec}^{-1}$  and  $H=238 \text{ KOe}$  are close to those



**Fig. 1.** Mössbauer absorption spectra (source:  $\text{Co}^{57}$  in Pd). (a).  $\text{Fe}_2\text{GeO}_4$  at  $f_{\text{O}_2}$  defined by FQM buffer. (b).  $\text{Fe}_2\text{GeO}_4$  at  $f_{\text{O}_2}$  defined by IW buffer. (c). Metallic iron.

reported for  $\text{Fe}_3\text{Ge}$  alloy (YAMAMOTO, 1965). For comparison the Mössbauer spectrum of Fe is given in Fig. 1c. When  $\text{Fe}_2\text{GeO}_4$  spinel was heated under atmospheric conditions at  $900^\circ\text{C}$ , it decomposed to  $\text{Fe}_2\text{O}_3$  and  $\text{GeO}_2$ .

The stability field of  $\text{Fe}_2\text{SiO}_4$  (olivine) is limited to the  $f_{\text{O}_2}$ , defined by the IQF (iron-quartz-fayalite) equilibrium boundary and FQM (fayalite-quartz-magnetite) equilibrium boundary. (EUGSTER and WONES, 1962, ERNST, 1962). Within the  $f_{\text{O}_2}$ , defined by WM (wüstite-magnetite) and FQM buffers, both  $\text{Fe}_2\text{GeO}_4$  and  $\text{Fe}_2\text{SiO}_4$  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  $f_{\text{O}_2}$ . No

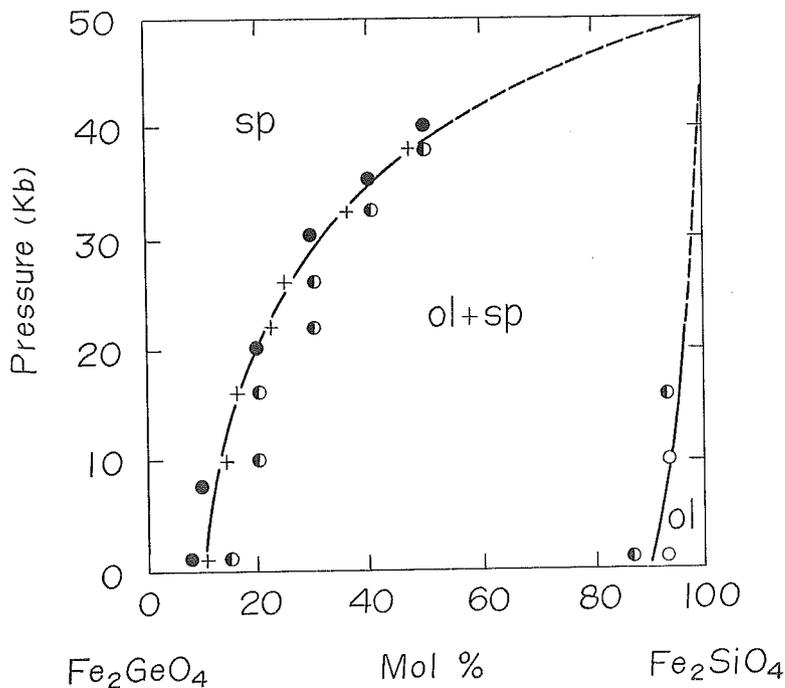


Fig. 2.

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

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

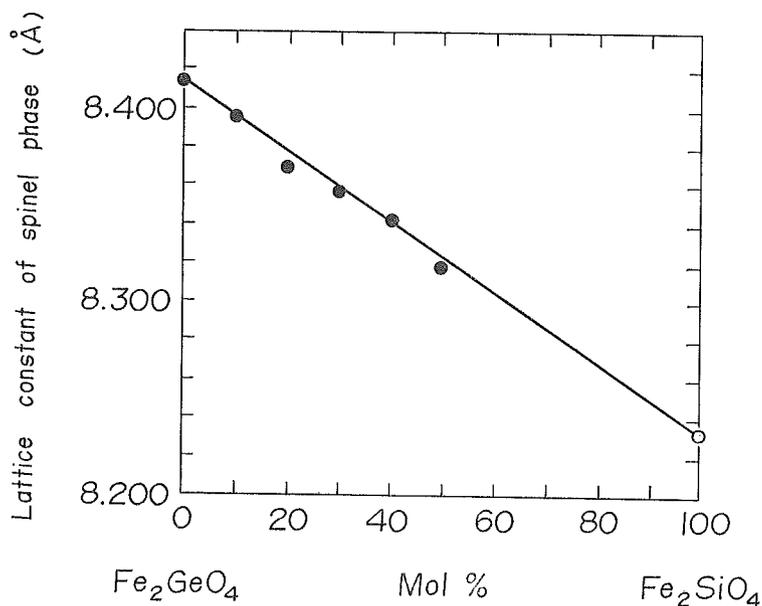


Fig. 3.

Change of lattice constant with composition of the  $\text{Fe}_2\text{GeO}_4$ - $\text{Fe}_2\text{SiO}_4$  spinel solid solution. (The value of  $\text{Fe}_2\text{SiO}_4$  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  $800^\circ\text{C}$  in the system  $\text{Fe}_2\text{GeO}_4$ - $\text{Fe}_2\text{SiO}_4$  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  $\text{Fe}_2\text{GeO}_4$ . They are plotted as a function of the mole fraction of Si in the spinel phase of the  $\text{Fe}_2\text{GeO}_4$ - $\text{Fe}_2\text{SiO}_4$  system in Figure 3. All points fall virtually on a straight line connecting the unit cell edge of  $\text{Fe}_2\text{GeO}_4$  spinel determined in this work and the corresponding value for  $\text{Fe}_2\text{SiO}_4$  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  $\text{Mg}_2\text{GeO}_4$ , which converts from the spinel form into the olivine form above  $810^\circ\text{C}$  and at atmospheric pressure (DACHILLE and ROY, 1961),  $\text{Fe}_2\text{GeO}_4$  synthesized hydrothermally at  $900^\circ\text{C}$  and 500 bars in this experiment is a normal

spinel. The spinel form of  $\text{Fe}_2\text{GeO}_4$  has been reported to exist at  $1,000^\circ\text{C}$  in vacuum (MATHUR et al., 1965). Mössbauer spectra of the synthesized  $\text{Fe}_2\text{GeO}_4$  indicate that within its stability range (from  $f_{\text{O}_2}$  defined by wüstite-magnetite buffer up to  $f_{\text{O}_2}$  defined by magnetite-hematite buffer at  $800^\circ\text{C}$ ), 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  $\text{Fe}_3\text{O}_4$ , 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  $f_{\text{O}_2}$  defined by fayalite-quartz-magnetite buffer, both  $\text{Fe}_2\text{GeO}_4$  and  $\text{Fe}_2\text{SiO}_4$  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  $700^\circ\text{C}$  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  $700^\circ\text{C}$ .

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  $700^\circ\text{C}$ .

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  $\text{Fe}_2\text{SiO}_4$  were observed in this work up to the pressure of 40 kilobars at  $800^\circ\text{C}$ . 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  $\text{Fe}_2\text{SiO}_4$  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  $800^\circ\text{C}$  for the olivine-spinel transition of fayalite.

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