[From PROCEEDINGS OF THE JAPAN ACADEMY, Vol. 42, No. 5 (1966)]

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By

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110. *Preliminary Experiments on the Stability of Natural Pigeonite and Enstatite*

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(Comm. by Chuji TSUBOI, M.J.A., May 12, 1966)

Introduction. Ca-poor pyroxenes, which range in composition from enstatite ($MgSiO_3$) to ferrosilite ($FeSiO_3$) through intermediate members, have two polymorphic forms, orthorhombic and monoclinic. They usually contain small amounts of Ca, Al, and certain other elements in solid solution. Because of the importance in petrology, the stability relation between the orthorhombic and monoclinic forms has been studied experimentally by many investigators. Bowen and Schairer (1935) studied the join $MgSiO_3$-$FeSiO_3$ as part of their studies on the system MgO-FeO-SiO_2, and have shown that monoclinic form is stable at higher temperatures than orthorhombic form. The inversion temperature decreases from 1140°C for pure $MgSiO_3$ to 955°C for $En_{12}Fs_{88}$ (weight percent). Foster (1951) found in his studies on the polymorphism of pure enstatite that a new polymorph is stable at high temperatures instead of clinoenstatite. This new polymorph is named protoenstatite, which has orthorhombic form (Smith, 1958). Atlas (1952) discussed that protoenstatite and orthoenstatite are high- and low-temperature forms, respectively, and that clinoenstatite is a metastable form. Boyd and Schairer (1964) discussed that clinoenstatite may be formed from protoenstatite on cooling from high temperatures. Sclar *et al.* (1964) found, however, that clinoenstatite has a stability field at lower temperatures than orthoenstatite. The inversion takes place at about 540°C at 1 atm and about 600°C at 20 kb (kilobars). Boyd and England (1965) confirmed this relation, although the inversion temperature obtained by them is about 100°C higher than that by Sclar *et al.* Akimoto *et al.* (1965a) and Lindsley (1965) have shown the same stability relation in ferrosilite, that is, orthoferrosilite is stable at higher temperatures than clinoferrosilite both of which are stable only at high pressures. Lindsley (1965) reported that the same stability relation is also held in the intermediate compositions between $MgSiO_3$ and $FeSiO_3$. Natural Ca-poor pyroxenes, however, contain various cations in addition to Mg and Fe^{2+} which may affect the stability relation of orthorhombic and monoclinic forms. Yoder *et al.* (1964)

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made experiments on natural pigeonites and subcalcic augites near the solidus temperatures at 1 atm. However, no experiment has been made on the stability of natural pigeonite and enstatite at relatively low temperatures. In the present experiments the polymorphism of natural pigeonite and enstatite has been studied at relatively low temperatures to compare the results with the synthetic systems.

Experimental procedures. Most runs of the present experiments have been made in the temperature range 590 to 1520°C and in the pressure range 20 to 45 kb, using a tetrahedral anvil type high-pressure apparatus which has been described by Akimoto *et al.* (1965b). Iron, molybdenum, and graphite capsules were used as sample containers. Pressure values were calibrated with the resistance phase transitions BiI-BiII, TlII-TlIII, and BaII-BaIII. Precision of pressure measurement and control for each run is about ±0.5 kb. Temperatures were measured with a Pt/Pt-13 Rh thermocouple. No correction was made for the effect of pressure on the emf of the thermocouple. Precision of temperature measurement and control is about ±10°C in each run. Two runs were made at 0.7 and 2.4 kb with a cold-seal type of hydrothermal quenching apparatus, and other two runs were made at 1 atm. The starting materials are pigeonite from andesite at Usugoya-zawa, Hakone Volcano, described by Kuno and Nagashima (1952) and orthoenstatite from harzburgite at Kamogawa, southeast of Tokyo (Kuno, 1954). Their chemical compositions and optical properties are shown in Table I. The phases after the runs were identified by both petrographic microscope and X-ray powder diffraction patterns.

Table I. Chemical compositions and optical properties of pigeonite and orthoenstatite used as starting materials in the present experiments.

	I	II
SiO_2	52.84	57.63
TiO_2	0.22	tr.
Al_2O_3	0.44	1.20
Fe_2O_3	1.06	0.32
FeO	16.89	3.20
MnO	0.56	0.02
MgO	23.51	36.07
CaO	4.06	0.89
Na_2O	0.19	n.d.
K_2O	0.00	n.d.
$H_2O(+)$	n.d.	n.d.
$H_2O(-)$	0.22	n.d.
P_2O_5	n.d.	none
Total	99.99	99.93
α(ave.)	1.695	1.660
β(ave.)	1.698	1.664
γ(ave.)	1.722	1.669
$2V$(ave.)	+14°	+68°

I Pigeonite in hypersthene-olivine andesite from Usugoya-zawa, eastern caldera wall of Hakone Volcano (Kuno and Nagashima, 1952).

II Orthoenstatite in harzburgite from Kamogawa, southeast of Tokyo (Kuno, 1954).

Experimental results. *Experiments on pigeonite.* The experiments on the Usugoya-zawa pigeonite were made at 40 and 41 kb in the temperature range 720 to 1500°C. The results are shown in Table II. At temperatures lower than 800°C at 41 kb, pigeonite is unchanged for 2 hour run. At 900°C at the same pressure, however, pigeonite is inverted to orthorhombic form for 2 hour run, and at temperatures higher than 1200°C and up to 1500°C at 40 kb, to orthorhombic form for 1/3-1 hour runs. The material inverted from pigeonite shows straight extinction and birefringence lower than that of the original pigeonite under the microscope. The refractive indices of the inverted material are as follows: $\gamma_{\max} = 1.710 \pm 0.002$, $\alpha_{\min} = 1.689 \pm 0.002$. Comparing the indices of the original pigeonite with those of the inverted material both $\gamma_{\max}$ and $\alpha_{\min}$ become lower after the inversion, and the birefringence becomes smaller. No exsolution lamellae of augite are found in the inverted material. The X-ray powder diffraction patterns of the inverted material are distinctly different from those of the original pigeonite, being similar to those of orthoenstatite. Fig. 1 shows the patterns of unchanged pigeonite and inverted material. The peaks of (420), (610), and (131) reflections are clearly shifted to higher angle and the (421) reflection appears

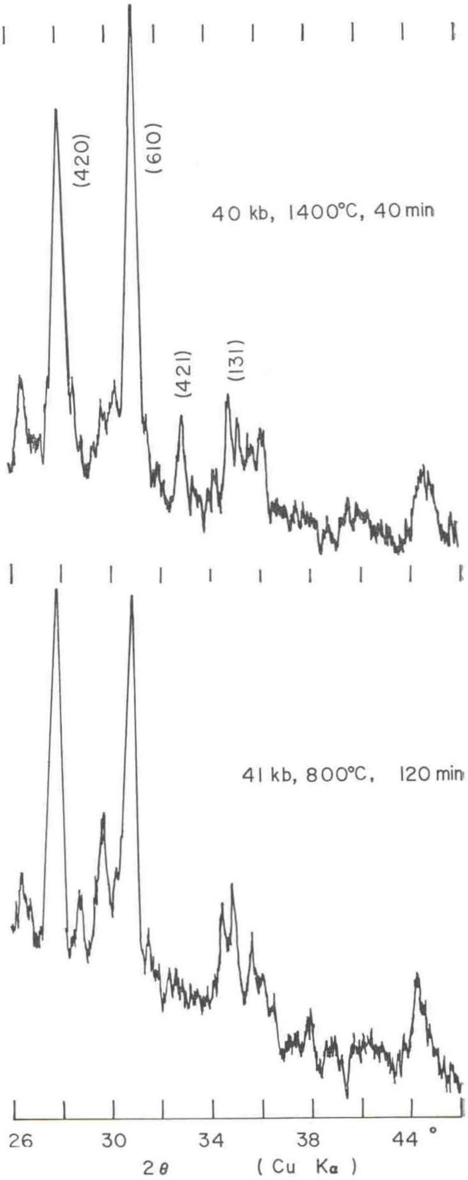

Fig. 1. Typical X-ray spectrometer patterns showing the inversion of natural pigeonite.
Upper figure: material inverted from pigeonite
Lower figure: unchanged pigeonite

Table II. Results of experiments with Usugoya-zawa pigeonite

Pressure (kb)	Temperature (°C)	Time (min)	Capsule	Results
40	1200	60	graphite	orthorhombic
40	1300	60	graphite	orthorhombic
40	1400	40	graphite	orthorhombic
40	1500	20	graphite	orthorhombic
41	720	150	graphite	unchanged
41	800	120	graphite	unchanged
41	900	120	graphite	orthorhombic

after the inversion. These indices are based on the orthorhombic symmetry. The Mg/Fe ratio of the material inverted from pigeonite is roughly estimated to be $En_{68}Fs_{32}$-$En_{64}Fs_{36}$ (mol. percent), using refractive indices-composition diagram prepared by Kuno (1954) on the assumption that the effect of Ca content on refractive indices of orthopyroxene is small. Comparing the composition of the inverted material with that of the original pigeonite, it is suggested that little oxidation or reduction of iron in pigeonite took place during the runs. From these experiments, it is indicated that pigeonite is stable at lower temperatures, whereas it is unstable at higher temperatures and is inverted to orthorhombic form. Although the inversion curve of the pigeonite has not been determined, the inversion temperature at 41 kb would be between 800 and 900°C.

Experiments on enstatite. The experiments on the Kamogawa enstatite were made in the temperature range 500 to 1520°C and in the pressure range 1 atm to 45 kb. The results are shown in Table III. The orthoenstatite is inverted to monoclinic form at 30 kb at 620°C for 3 hours, at 32 kb at 600°C for 2 hours, and at 32 kb at 855°C for 1 hour, using molybdenum capsule with water. Under the microscope the material inverted from orthoenstatite shows oblique extinction. The extinction is, however, not sharp but wavy in most crystals. Lamellar twinning was observed in some crystals. The refractive indices of the inverted material are as follows: $\gamma_{max}=1.671\pm0.002$, $\alpha_{min}=1.656\pm0.002$. These values are almost same as those of the original orthoenstatite. The inverted material shows, a different X-ray powder diffraction pattern from that of the original orthoenstatite, being same as that of clinoenstatite. The most conspicuous difference is the absence of the (421) reflection in the inverted material. The (421) reflection, of which 2θ is about 33° by CuKα radiation, is one of the characteristic reflections of orthoenstatite and is absent in the clinoenstatite reflections. The orthoenstatite-clinoenstatite inversion temperature

Table III. Results of experiments with Kamogawa enstatite

Pressure (kb)	Temperature (°C)	Time	Capsule	Results
0 (1 atm)	500	20 hr	Pt	unchanged
0 (1 atm)	590	20 hr	Pt	unchanged
0.7	570	20 hr	Au	unchanged
2.4	590	93 hr	Au	unchanged
20	590	120 min	Fe with H_2O	unchanged
21	1000	30 min	Mo	unchanged
30	620	180 min	Mo with H_2O	clinoenstatite
32	600	120 min	Mo with H_2O	clinoenstatite
32	855	60 min	Mo with H_2O	clinoenstatite
32	1000	30 min	Mo	unchanged
32	1000	30 min	Mo with H_2O	unchanged
32	1100	30 min	Mo with H_2O	unchanged
32	1185	20 min	Mo	unchanged
32	1520	6 min	Mo	unchanged
45	890	45 min	Fe with H_2O	unchanged
45	1000	30 min	Fe with H_2O	unchanged

is between 855 and 1000°C at pressures near 30 kb. It is higher than the inversion temperature at the same pressure for pure $MgSiO_3$ by Boyd and England (1965). The orthoenstatite was, however, not inverted to clinoenstatite at 20 kb at 590°C for 2 hours. At temperatures higher than about 890°C, the orthoenstatite was not inverted to clinoenstatite at pressures between 21 and 45 kb.

To confirm the inversion at low pressures, the orthoenstatite was heated at 500 and 590°C at 1 atm for 20 hours, at 570°C at 700 bars for 20 hours, and at 590°C at 2.4 kb for 93 hours. However, no change of the orthoenstatite took place.

Discussion. The present experiments indicate that orthorhombic form is stable at higher temperatures than monoclinic form in natural Ca-poor pyroxenes at high pressures. The results are, at least, qualitatively consistent with the results on synthetic pure $MgSiO_3$ by Sclar *et al.* (1964) and Boyd and England (1965), and those on $(Mg, Fe)SiO_3$ by Lindsley (1965). At pressures less than 5 kb, however, it is still uncertain whether these stability relations are valid or not. Boyd and England (1965) have shown that the inversion takes place at 5 kb at about 650°C for pure $MgSiO_3$. In the present experiments, no inversion took place at 2.4 kb at 590°C for about 4 days and 0.7 kb at 570°C for 20 hours, and at 500 and 590°C at 1 atm for 20 hours. This may indicate that the inversion is very sluggish at low pressures, and that higher pressure and/or longer time is required for the inversion. Another possibility is that the