neath the conti-
graph 10, 620.
.
physics 24, 262.
BERT (1968) Am.

trological nature
inhart and T. J.
, Am. Geophys.

egie Inst. Wash.

exploration of a
rust of the Earth,

es, Proc. Intern.
, Intern. Assoc.

ure 208, 271.

STABILITY AND STRUCTURAL RELATIONS OF (Mg, Fe) METASILICATES

TH. ERNST and R. SCHWAB

Mineralogisches Institut, Universität Erlangen-Nürnberg, Erlangen, West Germany

The polymorphism of $MgSiO_3$ and $MgSiO_3$–$FeSiO_3$ solid solutions, which are widespread in nature, has been the subject of numerous investigations which have obtained very contradictory results as to the number of modifications, their fields of stability and their structures (fig. 1).

As we now know, these diverse findings can be explained mainly on two facts, namely the use of starting materials of different origin and chemical composition, and the difficulties in identifying the polymorphs on the basis of their similar X-ray powder patterns.

Following HARALDSEN (1930) we shall interpret as protoenstatite the phase which is formed when talc is calcined, particularly the technical product which contains excess silica and some iron. To find out the stability relations it seemed necessary to use pure $MgSiO_3$, a compound which can be synthetized from the respective oxides MgO and SiO_2 in a ratio one to one.

On heating, the primary products are olivine and cristobalite, which transform slowly to the metasilicate at temperatures between 1450 and 1550 °C. It is necessary to grind the material several times. Subsequent annealing at about 1000 °C will give pure $MgSiO_3$ in which olivine or cristobalite can no longer be detected by X-ray or optical methods. The material synthetized in this way is monoclinic and corresponds both optically and in its X-ray pattern to clinoenstatite (MORIMOTO, *et al.*, 1960). On heating, clinoenstatite can be transformed to protoenstatite at 1260 ± 10 °C, and the protoenstatite remains unchanged up to the point of incongruent melting at 1555 °C. The powder patterns within this region are identical with those of protoenstatite formed from talc. Thus it is clear that the term protoenstatite is correct for the high-temperature modification of $MgSiO_3$.

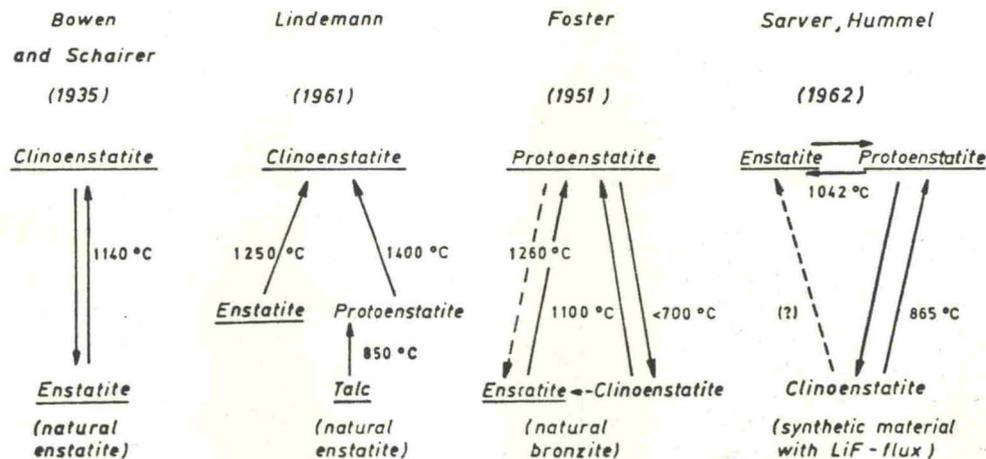Protoenstatite, formed from pure $MgSiO_3$ at tem-

Fig. 1. Polymorphism of $MgSiO_3$ according to BOWEN and SCHAIRER (1935), LINDEMANN (1960), FOSTER (1951) and SARVER and HUMMEL (1962). Modifications regarded as stable are underlined. The starting materials are given in parentheses.
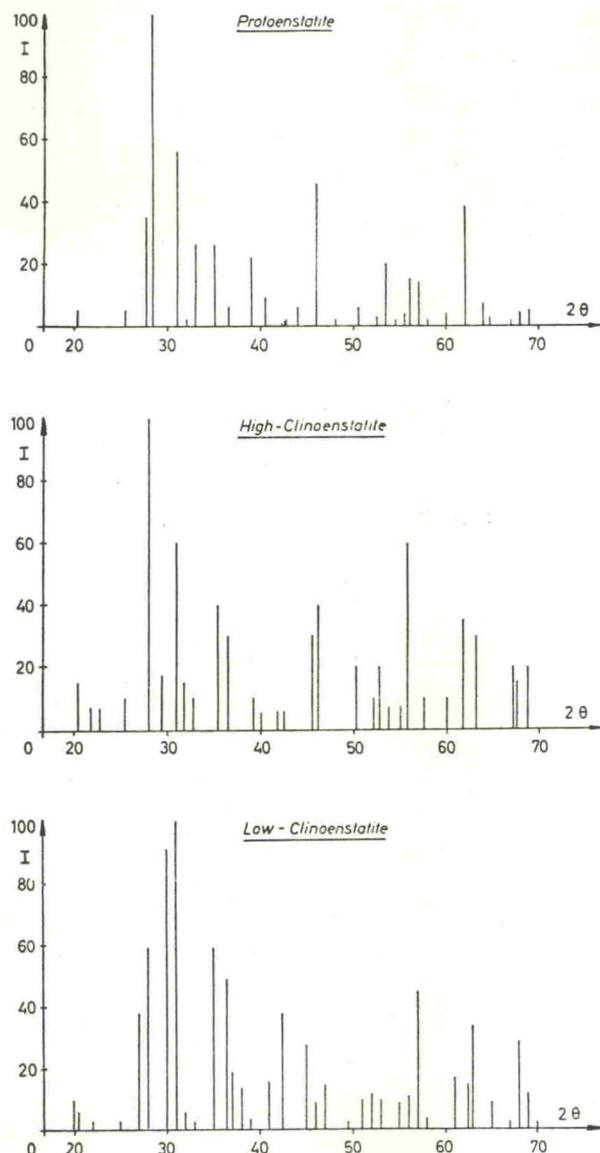
Fig. 2.   X-ray powder patterns of low-clinoenstatite, high-clino-
enstatite (1145 °C) and protoenstatie (from talc) (CuK$_z$ radiation).

peratures above 1260 °C, can be quenched only par-
tially, and commonly transforms spontaneously to cli-
noenstatite at room temperature. This contrasts with
the behaviour of protoenstatites formed from talc,
which are stabilized by excess silica.

We may remember now that protoenstatite is formed
reversibly at 1260 ± 10 °C. A detailed investigation,
however, reveals that this phase transformation does
not originate from unchanged clinoenstatite but from
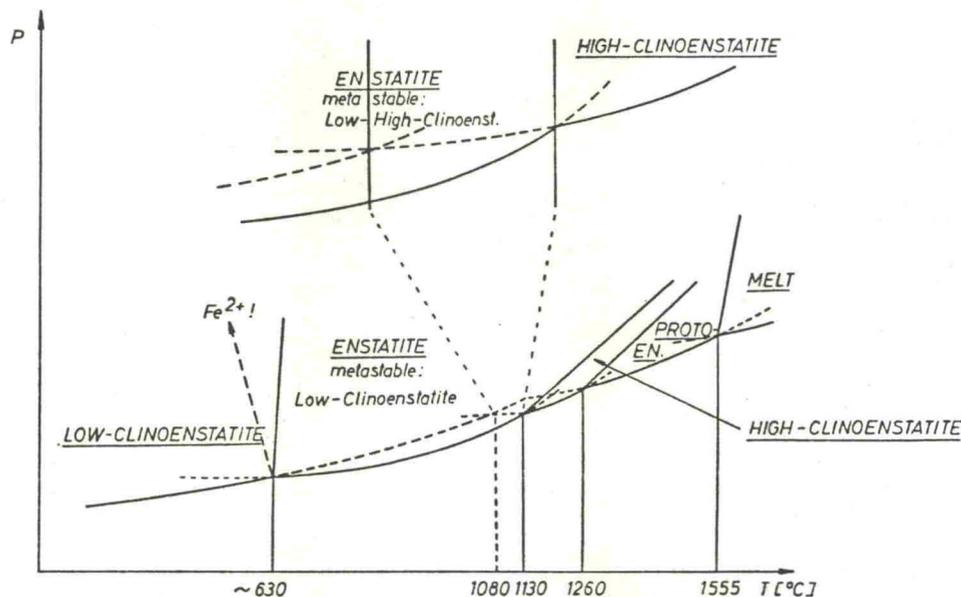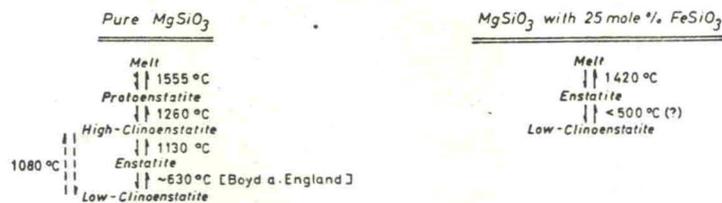a transitional phase which comes into existence at

1080 ± 10 °C. Clinoenstatite, henceforth more exactly
called low-clinoenstatite, transforms at 1080 °C to a
phase whose X-ray powder pattern is very similar to
that of protoenstatite, but also exhibits some analogies
to the diagram of low-clinoenstatite, as fig. 2 demon-
strates. Nevertheless, there exist some characteristic dif-
ferences which make an unequivocal identification pos-
sible: for example, the transitional phase has an addi-
tional reflection at $d = 3.06$ Å ($T = 1145$ °C), which
never appears in protoenstatite (SMITH, 1959). Moreover
there are some differences also at higher diffraction
angles, like splitting of reflections and differences in in-
tensities, which will not be discussed further; in general
the X-ray powder patterns point to a close structural
relationship between the three phases.

The interpretation that there might exist a really poly-
morphic phase between 1080 and 1260 °C and that the
diagrams may not be interpreted as a result of order–
disorder transitions or of the metastable coexistence of
two or more phases, is supported by thermal analyses.
Besides normal DTA-methods we applied the "dyna-
mical differential-calorimetry" from *Schwiete* (DDK)
and found that the transitions could be fixed surprisingly
well in this way. In order to get distinct heat effects it
was necessary to take pure and well crystallized samples
which had been stored for several months. In this con-
nection it is important to point out that the poly-
morphic behaviour of the substances is influenced by
their chemical composition and thermal history.

The field of the transitional phase is separated by
reversible and discontinuous heat effects from the fields
of low-clinoenstatite and protoenstatite. The phase
therefore has to be regarded as another high-tempera-
ture polymorph of $MgSiO_3$. For the present it will be
called high-clinoenstatite, mainly because of its physico-
chemical behaviour. Unlike protoenstatite, high-clino-
enstatite is not quenchable, and we are not yet able to
stabilize it in any way. We believe that some previous
investigators may have detected this phase, too, but
unfortunately did not carry on their studies (BROWN
and SMITH, 1963) or perhaps may have regarded it as
protoenstatite or as low-clinoenstatite (PEROTTA and
STEPHENSON, 1965; LINDEMANN, 1960). Commonly
high-clinoenstatite can easily be taken as protoensta-
tite, especially if the identification is confined to lower
diffraction angles and to the stronger reflections.

We have not yet discussed the stability of the rhombic

more exactly
080 °C to a
ry similar to
me analogies
ig. 2 demon-
acteristic dif-
ification pos-
has an addi-
5 °C), which
9). Moreover
r diffraction
rences in in-
er; in general
se structural

a really poly-
and that the
ilt of order–
coexistence of
nal analyses.
d the "dyna-
viete (DDK)
l surprisingly
neat effects it
ized samples
. In this con-
at the poly-
nfluenced by
istory.
separated by
om the fields
The phase
igh-tempera-
ent it will be
f its physico-
:, high-clino-
ot yet able to
me previous
ise, too, but
lies (BROWN
egarded it as
PEROTTA and
Commonly
protoensta-
ned to lower
ections.
the rhombic

Fig. 3.   Schematic *P–T* diagram of MgSiO$_3$.

enstatite, which is commonly regarded as the stable low-temperature polymorph of MgSiO$_3$. The synthesis of pure rhombic MgSiO$_3$ is not possible at 1 atm. Therefore it is necessary to apply either hydrothermal conditions or high pressures. The synthesis of the pure rhombic enstatite described in this study, was performed at 25 kb and 1300 °C, starting with low-clinoenstatite.

If large quantities are needed, it is more convenient to synthetize the rhombic phase at 1 atm at about 960 °C with LiF or LiOH as a flux. These fluxes cause a marked lowering of the transition temperatures and an increase of the transformation enthalpies.

The calorimetric investigations revealed that the rhombic enstatite forms the phase of higher enthalpy and entropy with respect to low-clinoenstatite. Low-clinoenstatite should be stable below 600 °C, which is in good agreement with the transformation temperature of 630 °C, extrapolated by BOYD and ENGLAND (1965)

from high pressure experiments. Because enstatite is the less dense phase (as the lattice constants and the optical constants in table 1 demonstrate), high pressures will lead to an extension of the field of low-clinoenstatite to higher temperatures at the expense of the field of the orthopyroxene.

However, the latter will extend its field of stability

TABLE 1

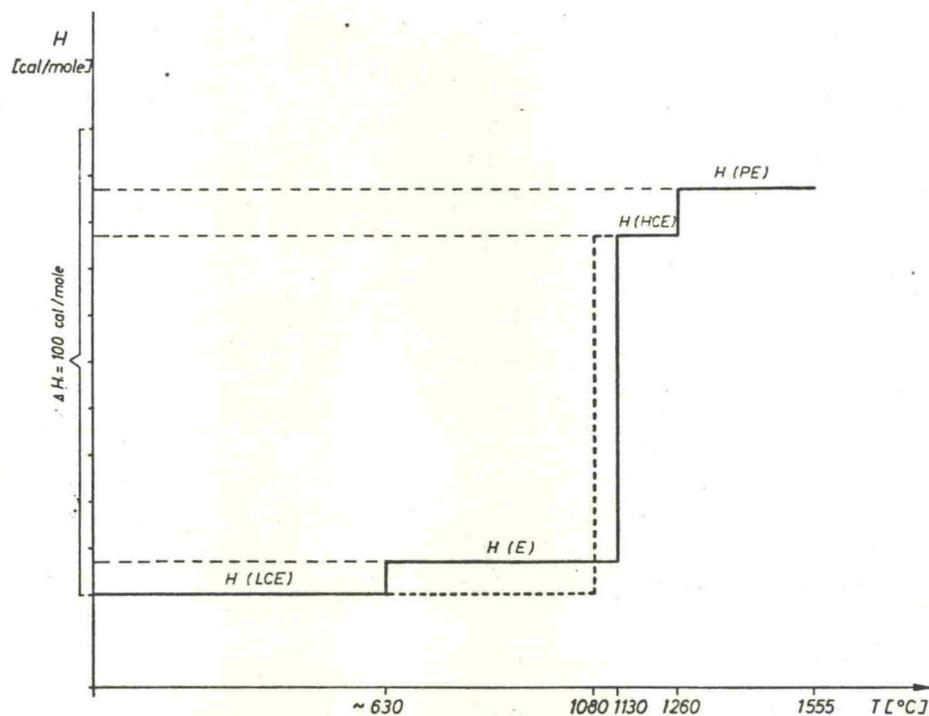| Pure synthetic enstatite:	Pure synthetic low-clinoenstatite:
optics:	
$n_x = 1.647$	$n_x = 1.650$
$n_\beta = 1.649$	$n_\beta = 1.653$
$n_\gamma = 1.657$ (R. Schwab)	$n_\gamma = 1.660$ (R. Schwab)
lattice constants:	
$a_0 = 18.203$ Å	$a_0 = 9.604$ Å
$b_0 = 8.807$ Å	$b_0 = 8.815$ Å
$c_0 = 5.202$ Å	$c_0 = 5.170$ Å $\beta = 71.65°$
$\frac{1}{2}V = 416.97$ Å^3	$\frac{1}{2}V = 415.47$ Å^3 (PEROTTA and
(R. SCHWAB)	STEPHENSON, 1965)

Fig. 4.   The transition enthalpies for pure $MgSiO_3$. All data are referred to the enthalpy of the α–β-quartz transition ($= 86$ cal/mole) according to MAJUMDAR *et al.* (1964).

against the fields of the high-volume phases high-clino-enstatite and protoenstatite which finally will vanish. These relations are presented schematically in fig. 3. Fig. 4 gives the transition enthalpies for pure $MgSiO_3$.

The presence of ferrous iron affects the stability of $MgSiO_3$ in the same way as increasing pressure, causing a marked increase in thermal stability of the rhombic enstatite relative to the high-temperature phases high-clinoenstatite and protoenstatite. At a content of 25 mole % of $FeSiO_3$ the orthopyroxene melts without any previous polymorphic transition (SCHWAB, 1967). However, there are some indications from the measured transformation enthalpies, that the field of the rhombic enstatite might also be extended against the field of low-clinoenstatite to lower temperatures. This assumption is supported by the high pressure experiments of AKIMOTO *et al.* (1965) in pure $FeSiO_3$.

The synthesis of orthopyroxenes at 1 atm is easily achieved in the system $MgSiO_3$–$FeSiO_3$ if it is per-formed under partial pressures of oxygen which pre-serve all iron in the bivalent state. It is also possible (as in LiF-containing systems) to demonstrate the re-versibility of the transition from high-clinoenstatite to

enstatite: slow cooling will lead to enstatite in an exo-thermal transformation, rapid cooling or quenching will lead to low-clinoenstatite in an exothermal, but at first metastable reaction (fig. 3).

Conclusions

Contrary to previous results the existence has to be assumed of at least one more high-temperature modi-fication of $MgSiO_3$. This polymorph is not identical with the high-clinoenstatite described by PEROTTA and STEPHENSON (1965) especially in Ca-containing prod-ucts.

Moreover there is the very important result, that Fe^{2+} will influence the polymorphism of $MgSiO_3$ in the same sense as pressure in the high temperature region. It is remarkable that the maximum stability of the rhombic phase exists at 1 atm at a content of about 25 mole % $FeSiO_3$ in the system $MgSiO_3$–$FeSiO_3$.

The structure determination of the high-clinoensta-tite modification described here will probably be still more difficult than with protoenstatite, where it is possi-ble to synthetize stabilized single crystals out of talc (LINDEMANN, 1951). Because high-clinoenstatite has its

position in between the fields of protoenstatite and low-clinoenstatite on one hand and protoenstatite and enstatite on the other hand, it would be very informative to have an exact knowledge about the structures of the respective end members. In the case of the rhombic enstatite exact and concordant structure analyses are available (WARREN and MODELL, 1930; LINDEMANN, 1961), but there is a controversy on the structures of low-clinoenstatite and protoenstatite between MORIMOTO *et al.* (1960) and SMITH (1959) on one side and LINDEMANN (1960) on the other side. Thus a new structural investigation of the polymorphs of $MgSiO_3$ seems to be necessary. These investigations have been started.

References

AKIMOTO, S., T. KATURA, Y. SYONO, H. FUJISAWA and E. KOMADA (1965) Polymorphic transitions of pyroxenes $FeSiO_3$ and $CoSiO_3$ at high pressures and temperatures, J. Geophys. Res. **70**, 5269–5278.

BOWEN, N. L. and J. F. SCHAIRER (1935) The system $MgO–FeO–SiO_2$, Am. J. Sci. **29**, 151–217.

BOYD, F. R. and J. L. ENGLAND (1965) The rhombic enstatite-clinoenstatite inversion, Ann. Rept. Geophys. Lab. Carnegie Inst. Wash. 1964–1965, 117–120.

BROWN, W. L. and J. V. SMITH (1963) High-temperature X-ray studies on the polymorphism of $MgSiO_3$, Z. Krist. **118**, 186–212.

FOSTER, W. R. (1951) High-temperature X-ray diffraction study of the polymorphism of $MgSiO_3$, J. Am. Ceram. Soc. **34**, 255–259.

HARALDSEN, H. (1930) Beiträge zur Kenntnis der thermischen Umbildung des Talks, Neues Jahrb. Mineral., Abhandl., Beilage Band **61 A**, 139–164.

LINDEMANN, W. (1960) Strukturuntersuchung der Kettensilikate unter besonderer Berücksichtigung der Mg-Pyroxene, Habilitationsschrift, Universität Erlangen.

LINDEMANN, W. (1961) Beitrag zur Enstatitstruktur (Verfeinerung der Parameterwerte), Neues Jahrb. Mineral., Monatsh. (10), 226–233.

LINDEMANN, W. (1961) Gitterkonstanten, Raumgruppe und Parameter des γ-$MgSiO_3$. Naturwissenschaften **48** (11), 428–429.

LINDEMANN, W. (1951) Darstellung und Kristallstruktur des γ-$MgSiO_3$, Dissertation (Univ. Erlangen).

MAJUMDAR, A. J., H. A. MCKINSTRY and RUSTUM ROY (1964) Thermodynamic parameters for the α-β-quartz and α-β-cristobalite transitions, J. Phys. Chem. Solids **25**, 1487–1489.

MORIMOTO, N., D. E. APPLEMAN and H. T. EVANS, JR. (1960) The crystal structure of clinoenstatite and pigeonite, Z. Krist. **114**, 120–147.

PEROTTA, A. J. and D. A. STEPHENSON (1965) Clinoenstatite: High-low inversion, AAAS 148, 1090–1091.

SARVER, J. F. and F. A. HUMMEL (1962) Stability relations of magnesium metasilicate polymorphs, J. Am. Ceram. Soc. **45**, 152–156.

SCHWAB, R. G. (1967) Die Bedeutung und die experimentelle Beherrschung des Sauerstoffpartialdruckes bei der Synthese und Untersuchung Fe^{2+}-haltiger Silikate, Neues Jahrb. Mineral., Monatsh. (7/8), 244–254.

SMITH, J. V. (1959) The crystal structure of protoenstatite $MgSiO_3$, Acta Cryst. **12**, 515–519.

WARREN, B. E. and D. I. MODELL (1930) The structure of enstatite $MgSiO_3$, Z. Krist. **75**, 1–14.

= 86 cal/mole)

e in an exo-
quenching
rmal, but at

ce has to be
ature modi-
ot identical
EROTTA and
ining prod-

result, that
$MgSiO_3$ in
temperature
stability of
ent of about
FeSiO_3.
-clinoensta-
ably be still
re it is possi-
out of talc
atite has its