obtained from the worked surface. The example shown in Fig. 2*c*, an early Persian seal of the Sassanian Period (A.D. 200 to 600) is a shallow cut intaglio; this makes the least satisfactory impression photograph. On the combination print may be seen grinding traces which remained invisible not only on the impression but under direct inspection with a × 4 hand lens. This basically photographic technique has important applications to documentation in at least one field of archeological research.

C. A. Erskine
School of Anatomy, Trinity College, University of Dublin, Dublin, Ireland

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Clinoenstatite: High-Low Inversion

Abstract. *Clinoenstatite undergoes a metastable displacive inversion at 995°C. The new phase can be indexed (from x-ray powder pattern) on a triclinic cell with dimensions* $a = 10.00$ Å; $b = 8.934$ Å; $c = 5.170$ Å; *alpha* = 88.27°; *beta* = 70.03°; *gamma* = 91.09°. *The new phase persists from 995° to 1010°C at the composition* $MgSiO_3$. *For a solid solution (15 percent by weight) of diopside in clinoenstatite, the new phase persists from 995° to at least 1400°C and does not invert in periods of several hours to protoenstatite, the phase previously thought to be the stable form in this region.*

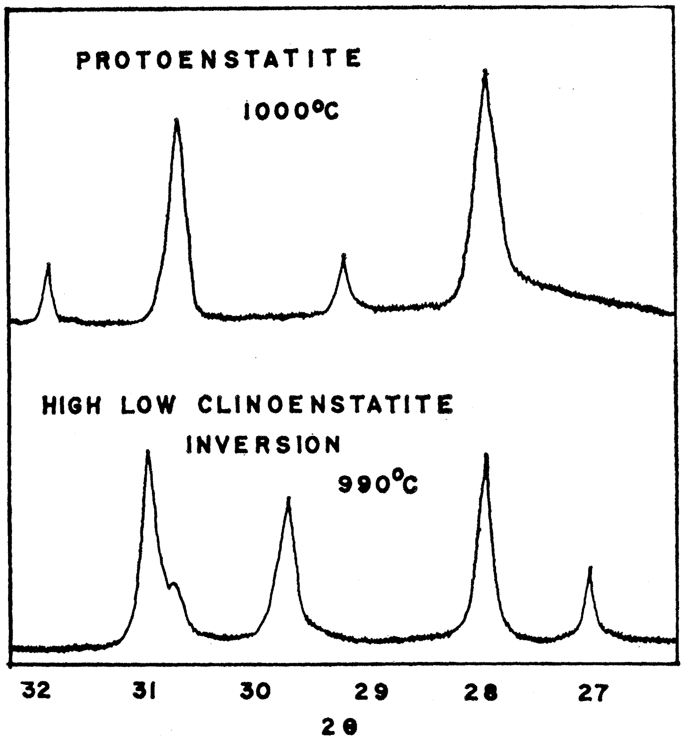
In spite of many studies, which have been reviewed elsewhere (*1*), over the past 15 years, the stability relations of the polymorphs of $MgSiO_3$ are still uncertain. To date, three principal polymorphs of $MgSiO_3$ have been described and indexed: orthoenstatite (*Pbca*), protoenstatite (*Pbcn*), and clinoenstatite ($P2_1/c$). Disordered forms of both orthoenstatite and clinoenstatite have been reported by Brown and Smith (*1*) and Byström (*2*). Boyd and Schairer (*3*) have presented the latest data on the enstatite-diopside system at atmospheric pressure. They find that phase relations on the "enstatite" side of the system are extremely difficult to determine if conventional quenching techniques are used. Because their complex and sometimes inconsistent findings may result from rapid inversion during quenching, we have attempted to determine the phase relations directly at high temperature with a Tem-Pres furnace (*4*) attached to a Norelco diffractometer. Our investigation was stimulated by Boyd and Schairer's discovery that some charges quenched from above 1385°C contained orthoenstatite, and their speculation on the presence of a new form of $MgSiO_3$ which inverted to orthoenstatite during the quenching. Their conjecture has not yet been proved or disproved by us because of the possibility of metastability, but it has led to the discovery of a new displacive-type inversion in clinoenstatite. This high form of clinoenstatite is probably the intermediate form which Foster (*5*) encountered, but unfortunately he was unable to reproduce his results which, as discussed below, are due to the narrow range of temperature in which this form exists in pure $MgSiO_3$.

The mixtures used in this study were supplied by F. R. Boyd (*6*). The glasses received from him were recrystallized by keeping them at 1350°C for 3 days in platinum crucibles in the absence of a catalyst and then by quenching in air. X-ray patterns of the material showed that, in accordance with the known stability relations, clinoenstatite was the only phase present at room temperature.

During a preliminary investigation of pure clinoenstatite, a marked splitting of the (310) reflection was noticed at about 1000°C, the approximate inversion temperature of clinoenstatite to protoenstatite (Fig. 1). However, further studies showed that the substitution of calcium in clinoenstatite raised the clinoenstatite-protoenstatite inversion temperature and thus permitted a full investigation of the (310) splitting. In fact, a solid solution (15 percent by weight) of diopside in clinoenstatite showed no formation of protoenstatite even at temperatures up to 1400°C, the upper limit of the apparatus. Further examination of this solid-soluiton sample showed that the (310) reflection split completely and rapidly over an interval of 10°C at approximately 1000°C, and that the splitting produced a new phase which persisted up to at least 1390°C. This phase, high clinoenstatite, apparently exists, at least for periods of 2 to 3 hours, in the temperature range formerly thought to be restricted to the protoenstatite form. A comparison of the x-ray patterns, where 2θ ranges from 26 to 32 deg, of high and low clinoenstatite of a diopside composition that is 15 percent

Table 1. X-ray diffraction data of powdered high clinoenstatite with nickel filtered copper radiation. *d*, Interplanar spacing; *I*, intensity; *hkl*, Miller indices.

d_{obs} (Å)	d_{calc} (Å)	I/I_0	*hkl*
6.43	6.38	2	110
5.19	5.08	2	101
4.47	4.46	17	020
4.12	4.11	33	210
3.94	3.98	10	120
3.76	3.76	3	$2\bar{1}1$
3.56	3.56	6	$\bar{1}\bar{1}1$
3.34	3.35	42	$0\bar{2}1$
3.22	3.23	76	021
3.06	3.05	100	221
2.98	2.98	30	$3\bar{1}0$
2.92	2.93	91	310
2.86	2.86	2	$\bar{1}30$
2.84	2.84	8	$\bar{1}\bar{2}1$
2.80	2.81	11	130
2.588	2.580	20	321
2.533	2.528	13	320
2.501	2.494	33	$0\bar{3}1$
2.456	2.459	20	212
	2.452		$1\bar{1}2$
2.296	2.299	6	$\bar{1}\bar{3}1$
2.167	2.165	30	331
	2.168		022
2.148	2.152	16	421
2.094	2.090	15	322
2.058	2.058	6	041
2.043	2.039	12	$\bar{2}40$
	2.040		$\bar{2}\bar{3}1$
2.012	2.011	6	$\bar{3}\bar{2}1$
1.975	1.972	8	241
1.943	1.943	3	511
1.815	1.818	8	430
1.806	1.808	7	$\bar{2}41$
1.782	1.784	10	$\bar{3}\bar{3}1$
1.759	1.755	12	$\bar{4}21$
1.699	1.697	3	151
	1.700		$4\bar{3}2$
1.647	1.647	27	441
	1.647		$\bar{3}12$
1.632	1.632	15	611
	1.629		342
1.611	1.612	6	$0\bar{4}2$
	1.611		$\bar{5}30$
1.5458	1.5458	10	$\bar{5}\bar{1}1$
1.5353	1.5346	4	610
1.5108	1.5108	11	$4\bar{2}3$
	1.5107		233
1.5068	1.5072	11	$\bar{5}21$
1.4931	1.4949	7	$\bar{2}\bar{5}1$
	1.4923		622
1.4328	1.4337	4	523
	1.4312		352
1.3916	1.3909	15	$\bar{2}03$
1.3777	1.3790	4	$7\bar{1}2$
1.3661	1.3665	7	$\bar{1}\bar{6}1$
	1.3655		$\bar{2}\bar{1}3$
	1.3652		343
1.3032	1.3032	3	$\bar{2}\bar{6}1$
1.2823	1.2325	7	314
	1.2821		$\bar{5}12$
1.2271	1.2267	4	$\bar{3}\bar{6}1$
	1.2273		811



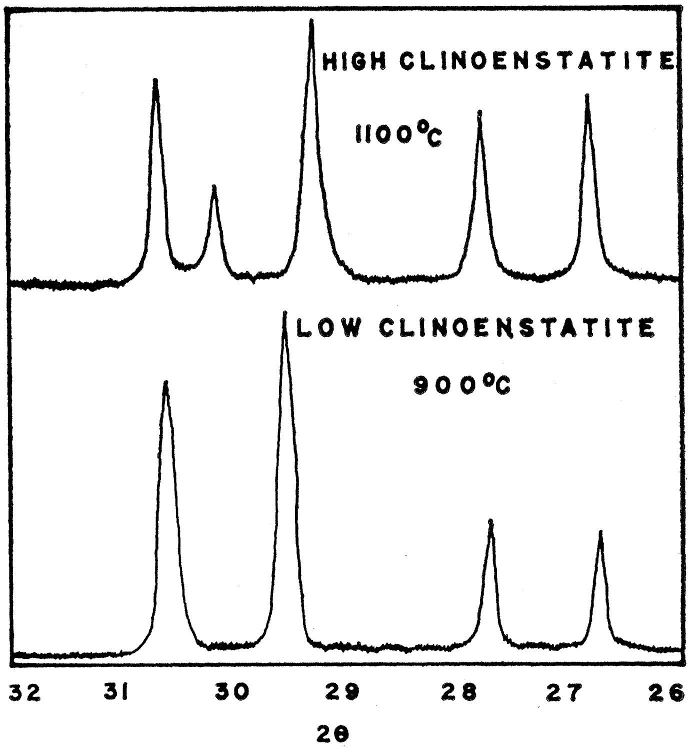


Fig. 1 (left). Splitting of the (310) clinoenstatite reflection at $2\theta = 31°$ moments before inversion to protoenstatite. Fig. 2 (right). Comparison of the high and low clinoenstatite x-ray powder patterns at high temperature.

Table 2. Comparison of the cell parameters of high and low clinoenstatite with platinum powder as an internal standard ($a_0 = 3.9231$ Å, $\alpha = 8.49 \times 10^{-6}$ per deg C).

Type	Edges (Å)			Angles (deg)			Volume (Å^3)
	a	*b*	*c*	alpha	beta	gamma	
Low	9.604 ± .001	8.815 ± .001	5.170 ± .001	90.00	71.65 ± .01	90.00	415.47 ± .09
High	10.000 ± .005	8.934 ± .004	5.170 ± .003	88.27 ± .05	70.03 ± .04	91.01 ± .04	433.78 ± .41

by weight is shown in Fig. 2. Additional study of a solid solution of diopside (10 percent by weight) in clinoenstatite also indicated that the protoenstatite polymorph does not appear even at a cut-off temperature of 1390°C, and that the high-low transformation temperature, found by cycling through the inversion point, is 995° ± 5°C.

A full x-ray pattern was made of the solid solution (10 percent by weight) of diopside at 1100°C with platinum powder as an internal standard. The pattern obtained was quite distinct from patterns of clinoenstatite. A preliminary indexing, based on the splitting of the (310) reflection and the persistence of other strong, low-angle reflections which survived the high-low transformation, furnished enough information for us to believe that the cell was triclinic, and this led to the indexing of all reflections. The x-ray data of powdered high clinoenstatite are presented in Table 1. The triclinic cell was refined by the method of cell-edge least squares from a computer program written by C. W. Burnham (*7*). The final cell parameters of high clinoenstatite are shown in Table 2 along with the cell parameters of low clinoenstatite which were obtained from a high-pressure ($T = 700°C$, $P = 75$ kb) sample prepared by C. Sclar (*8*) and refined by one of us (D.A.S.). Only a small change in cell geometry occurred, and this change is mainly parallel to the *ab* plane.

In conclusion, a metastable displacive transformation at about 995° ± 5°C in low clinoenstatite results in a new polymorph which is triclinic and which is now referred to as high clinoenstatite. This new form has its apparent stability field enlarged with increasing calcium content so that it appears to displace the protoenstatite field to higher temperatures. Because the high temperature of inversion of clinoenstatite to protoenstatite is raised very considerably with increased calcium content, the presumed equilibrium inversion temperature of orthoenstatite to protoenstatite also may be raised by a similar amount so that the activation energy required to create orthoenstatite is sufficient somewhere above 1390°C. This would mean that the orthoenstatite obtained in the quenching runs of Boyd and Schairer did not come from another polymorph, but actually existed above 1385°C. For testing true stability, special heating apparatus would be necessary to permit long runs (weeks) without quenching.

A. J. Perrotta
D. A. Stephenson
Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois

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