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Melting and Subsolidus Phase Relationships for $CaSiO_3$ to 35 Kilobars Pressure

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Abstract

Phase transitions between pseudowollastonite, wollastonite I, and wollastonite II have been reversed in piston-cylinder apparatus, and the melting curve for these $CaSiO_3$ polymorphs has been determined between 10 and 35 kbars. The pseudowollastonite melting curve rises from 1544°C at 1 bar with an unusually steep slope ($dP/dT = 580$ bar/°C) to a triple point at 1588°C and 23 kbar, where the solidus meets the transition from pseudowollastonite to wollastonite I, rising from 1125°C at 1 bar. The transition boundary between wollastonite I and wollastonite II has a shallow, negative slope ($dP/dT = -8.4$ bar/°C); the triple point where it reaches the solidus is at 1598°C and 27.5 kbar. The slope of the fusion curve decreases at each triple point, and dP/dT for wollastonite II, 192 bar/°C, is much closer to that of other silicates, such as diopside, enstatite, and albite, than to wollastonite I. Refractive indices of glasses quenched from high pressure $CaSiO_3$ and $CaMgSi_2O_6$ liquids vary less as a function of pressure than do indices of glasses quenched from feldspars and feldspathic liquids. Either the densities of liquids of inosilicates are changed less than those of tektosilicates by pressure, or their high pressure densities are not quenched into the glasses.

Introduction

When studying the liquidus relationships between silicates and carbonates in the system CaO–MgO–SiO_2–CO_2, Huang and Wyllie (1974) encountered a polymorph of $CaSiO_3$ on the liquidus at 30 kbar. This turned out to be the phase recently designated wollastonite II by Essene (1974), which had been discovered by Ringwood and Major (1967) and analyzed structurally by Tröjer (1968, 1969). In the process of determining the range of crystallization of wollastonite II we completed an experimental study of the melting relationships and subsolidus phase transitions between the polymorphs wollastonite II, wollastonite I, and pseudowollastonite.

Experimental Methods

The starting materials were crystalline wollastonite I ($\beta - CaSiO_3$), pseudowollastonite ($\alpha - CaSiO_3$), and wollastonite II. The stoichiometric composition of $CaSiO_3$ was prepared by mixing dry Ca_2SiO_4 gel and fired amorphous silica. This was crystallized with about 20 percent water in sealed gold capsules in a cold-seal pressure vessel at 700°C and 2 kbar for 4 days to yield wollastonite I, which was then fired to about 1100°C for 15 hours. This was converted to pseudowollastonite and wollastonite II as required, by subjecting it to appropriate pressures and temperatures. Starting materials were loaded in platinum capsules and dried at 500°C for more than one hour prior to sealing.

Experiments were performed in a ½-inch piston-cylinder apparatus. The furnace assembly is similar to that illustrated by Irving and Wyllie (1975), except that the fired boron nitride cylinder was replaced by a pyrex glass cylinder for runs at temperatures below 1450°C. All runs were brought to final pressure with "piston-out" procedure. Pressure was first set to about 2 to 3 kbar, the sample was heated to 950°C, the pressure was raised again to 6 kbar above the desired value, the sample was brought to desired temperature, and finally the pressure was released to the desired value.

According to Boyd *et al* (1967), the nominal pressure with this procedure is within 5 percent of the correct pressure, and therefore we have reported uncorrected nominal pressures. However, recent interlaboratory calibration studies on albite breakdown suggest that "anvil" or "shield" effects may occur at low temperatures (600°C) with this procedure, making nominal pressures higher than actual pressures (Bell and Mao, 1971). We do not know the extent to which this effect operates at higher temperatures and pressures, but to facilitate interlaboratory comparison we bracketed the quartz-coesite transition at

1100°C between nominal pressures 34 and 35 kbar, using the same furnace assembly and procedure as for the $CaSiO_3$ experiments. Essene (1974) pointed out that the wollastonite I–II transition is potentially useful as a pressure calibrant, if it can be reversed with a hydrostatic gas apparatus.

Temperatures, measured with calibrated W 5Re/W 26Re thermocouples, from Omega Engineering, Inc., are precise to ± 5°C and accurate to better than ± 15°C. In a test run at 1500°C and 30 kbar using two adjacent thermocouples, the temperature recorded by the W-Re thermocouple was 5°C higher than that recorded by the Pt/Pt 10Rh thermocouple.

Run products were analyzed using standard petrographic and X-ray powder diffraction techniques. Wollastonite I exhibited an elongate prismatic or acicular habit with lengths up to 120 microns. Pseudowollastonite grains were irregular with a refractive index close to 1.620. Wollastonite II crystals were euhedral and prismatic with refractive indices: $\alpha = 1.636$, $\beta = 1.653$, $\gamma = 1.662$ (accuracy ± 0.002). The measured *d* values of wollastonite II closely match those determined by Tröjer (1968, 1969; Borg and Smith, 1969).

Crystalline wollastonite polymorphs melt congruently to a liquid which quenches to clear isotropic glass, to "quench" crystals, or to a mixture of glass and quench crystals. The quench crystals were distinguished from the primary crystals by their irregular extinction. In the 30 kbar runs, the proportion of quench crystals to glass increases as a function of temperature, from a few quench crystals near the liquidus to all quench crystals at 50°C above liquidus.

TABLE 1. Results of Experiments for the Phase Relationships of $CaSiO_3$ Composition

Run*	Press. Kb	Temp. °C	Duration min.	Starting material wt.% Wo-I	Wo-II	PWo	Results
826	10	1375	210	100	0	0	PWo
891	10	1500	20	100	0	0	PWo
824	10	1550	10	100	0	0	PWo
823	10	1575	10	100	0	0	L
861	15	1500	30	100	0	0	PWo
825	15	1550	10	100	0	0	PWo
820	17.5	1550	10	100	0	0	Wo-I
835	17.5	1550	15	10	0	90	PWo
739	20	1525	15	100	0	0	Wo-I
869	20	1550	20	50	0	50	PWo
752	20	1560	15	100	0	0	Wo-I
740	20	1600	15	100	0	0	L
892	21	1550	20	50	0	50	PWo
846	22	1550	20	50	0	50	Wo-I
808	25	1500	10	100	0	0	Wo-I
862	25	1575	15	100	0	0	Wo-I
841	25	1600	15	100	0	0	L
832	26.5	1550	10	100	0	0	Wo-I
834	26.5	1550	15	10	90	0	Wo-I
809	27.5	1500	10	100	0	0	Wo-I
890	27.5	1550	15	50	50	0	Wo-I
830	28.5	1550	10	100	0	0	Wo-II
827	30	1100	23 hr	10	90	0	Wo-I
819T	30	1350	60 min	100	0	0	
	30	1200	120	100	0	0	Wo-II
821T	30	1350	60	100	0	0	
	30	1200	23 hr	100	0	0	Wo-II
799	30	1200	60 min	100	0	0	Wo-I
750	30	1300	30	100	0	0	Wo-II
763	30	1350	120	100	0	0	Wo-II
737	30	1420	5	100	0	0	Wo-II
889	30	1500	15	100	0	0	Wo-II
738	30	1550	15	100	0	0	Wo-II
856	30	1575	20	0	100	0	Wo-II
741	30	1600	15	100	0	0	L
842	30	1600	15	100	0	0	Wo-II
858	30	1600	15	0	100	0	L
735	30	1625	5	100	0	0	L
855	30	1625	20	0	100	0	L
744	30	1650	15	100	0	0	L
746	30	1700	5	100	0	0	L
893	31.25	1100	20 hr	50	50	0	Wo-I
811	32.5	900	180 min	100	0	0	Wo-I
812	32.5	1000	180	100	0	0	Wo-I
816	32.5	1100	90	100	0	0	Wo-I
818	32.5	1100	180	100	0	0	Wo-II
859	35	1625	15	0	100	0	Wo-II
860	35	1650	15	0	100	0	L

Abbreviations: Wo-I = wollastonite I; Wo-II = wollastonite-II; PWo = pseudowollastonite; L = liquid.

* T: Two-stage runs; sample held in the field of Wo-II at 1350°C for 60 min., then temperature reduced to desired value.

Experimental Results

Experimental runs are listed in Table 1 and plotted in Figure 1. At atmospheric pressure, wollastonite I transforms into pseudowollastonite at 1125°C and pseudowollastonite melts at 1544°C (Osborn and Schairer, 1941).

We defined the wollastonite I–pseudowollastonite transition with a reversed bracket between 21 and 22 kbar at 1550°C (runs 892 and 846), using a 50/50 mixture of the phases as starting material. Within the pseudowollastonite field, this mixture reacted completely in 20 min, whereas in some runs with wollastonite I as starting material, no pseudowollastonite nucleated at all in runs of 10 or 15 min (820 and 752).

The wollastonite I–II transition was reversed between 28.5 and 27.5 kbar at 1550°C in runs of 10 and 15 min (830 and 890). Starting materials of wollastonite I and a 50/50 mixture reacted completely to wollastonite II and to wollastonite I, respectively. For the other reversed bracket at 1100°C, reaction rates were slower. At 32.5 kbar wollastonite I did not change in 90 minutes, but in a 3 hour run it converted completely to wollastonite II (runs 816 and 818). At 1100°C and 31.25 kbar, a 50/50 mixture was converted completely to wollastonite I in 20 hours (run 893).

In the runs at 30 kbar, wollastonite I as starting material was transformed completely to wollastonite II in runs at 1300°C and above in 30 minutes or less. In two runs at 30 kbar (819 and 821) wollastonite I was first held in the stability field of wollastonite II, and then lowered to 1200°C without pressure change,

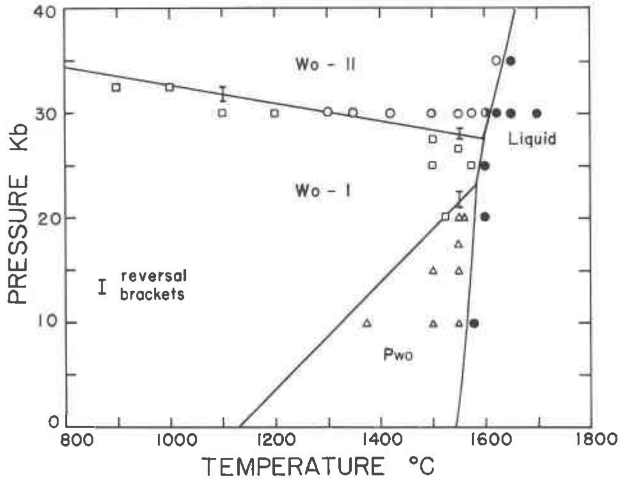

FIG. 1. Experimental results showing the subsolidus and melting relations for $CaSiO_3$. Solid circles denote runs above liquidus; open symbols denote subsolidus runs. The definitive reversal brackets on the subsolidus transitions are shown. Abbreviations: Wo-I, wollastonite I; Wo-II, wollastonite II; Pwo, pseudowollastonite.

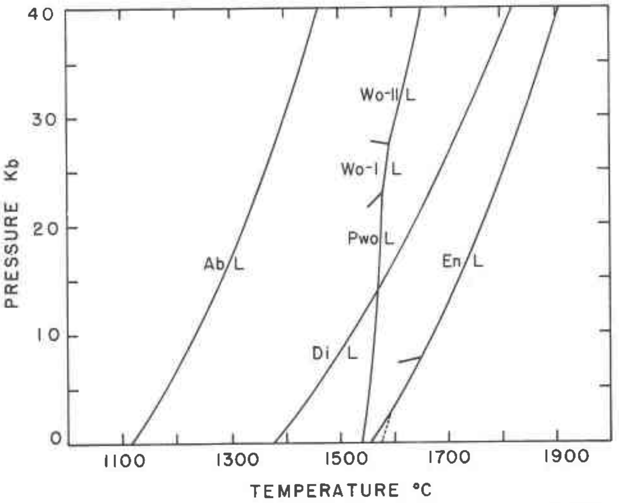

FIG. 3. Experimentally determined melting curves for $CaSiO_3$ (Fig. 1), diopside (Boyd and England, 1963), enstatite (Boyd, England, and Davis, 1964) and albite (Boyd and England, 1963).

where it should have been within the wollastonite I field, according to the reversed curve shown in Figure 1. Under these conditions, none of the wollastonite II was transformed back to wollastonite I in runs lasting for 2 hours and 23 hours. We conclude that, without seeding, the wollastonite I → II transformation takes place more readily than the reverse transformation.

The melting curve was bracketed at several pressures. Observation of melting in glass containing at most only a few quench crystals was easy up to 25 kbar. However, because of the abundance of quench crystals in glass at higher pressures, several runs at 30 kbar were required to establish unambiguous criteria for melting. Starting materials included wollastonite I and wollastonite II, to ensure that there was no complication involving metastable melting of wollastonite I. The slope of the melting curve changes at two triple points where the subsolidus phase boundaries meet the melting curve, at 23 kbar and 27.5 kbar.

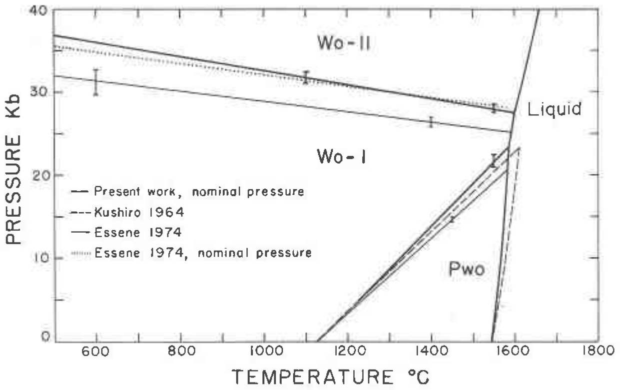

FIG. 2. Phase relations from Figure 1 compared with previous studies by Kushiro (1964) and Essene (1974).

Our reversals and phase boundaries from Figure 1 are compared in Figure 2 with results of Kushiro (1964) for the melting and transition of pseudowollastonite, and with those of Essene (1974) for the two subsolidus reactions. Our results are shifted to slightly lower temperatures than those of Kushiro, but they are effectively the same within the limits of experimental error. Essene's wollastonite I–wollastonite II curve is located by reversed brackets at 1400°C and 600°C; he used a piston-in method and applied a −10 percent correction to the pressure. Figure 2 shows Essene's results in terms of nominal pressures before applying the friction correction; they are identical with our nominal pressure results.

The indices of refraction of $CaSiO_3$ glasses measured in white light for run products quenched from above the liquidus increase linearly from 1.624 at atmospheric pressure to 1.641 at 35 kbar, with uncertainty of ± 0.002 (Fig. 4). The rate of increase in index with pressure on original liquid is small relative to rates determined for many other glasses from molten silicates and rocks, but is similar to that for diopside glass.

Discussion

The slope for the melting curve of pseudowollastonite averages 580 bar/°C, which is considerably steeper than those for many other sili-

TABLE 2. Comparison of Melting Curve Slopes for $CaSiO_3$, Diopside, Enstatite, and Albite

Phases	ΔV_f^o cm^3/mole	ΔS_f^o cal/mole°C	dP/dT bar/°C Calculated Initial slope at 1 bar	dP/dT bar/°C Measured experimentally Average slope	Pressure ranges Kb
Wo-II	-	-	-	192 (1)	27.5-35
Wo-I	-	-	-	346 (1)	23-27.5
PWo	1.580 (2,3)	7.375* (4)	193	580 (1)	0-23
Di	12.105 (2)	11.120 (5)	38	90 (6)	5-30
En	-	-	-	113 (7)	5-30
Ab	9.660 (2)	9.478 (5)	42	114 (8)	5-30

Numbers in parentheses indicate the sources of data:

(1)-present study; (2)-Clark (1966); (3)-Tomlinson (1958); (4)-Knapp and Flood (1961); (5)-Robie and Waldbaum (1968); (6)-Williams and Kennedy (1969); (7)-Boyd, et al (1964); (8)-Boyd and England (1963). For abbreviations see Figures 1 and 3.

*3.605 cal/mole°C according to Robie and Waldbaum (1968).

cates (Fig. 3; Table 2). The slope decreases at each triple point, and the value for wollastonite II is 192 bar/°C, which is much closer to the values for the other minerals tabulated. Table 2 compares the average slopes of the melting curves for several minerals, as determined experimentally at high pressures. The table also shows dP/dT for some of the melting curves at 1 bar pressure, as calculated from values for heats of fusion and volume changes on melting. These values are less steep than the high-pressure empirical curves.

The unusually steep melting curve for pseudowollastonite is caused by the small values for ΔV_f at the melting point, compared with ΔV_f for the other minerals listed in Table 2. The Table shows that ΔS_f for pseudowollastonite is also smaller than for the other minerals, but the calculated values for dP/dT confirm the dominant effect of the small ΔV_f.

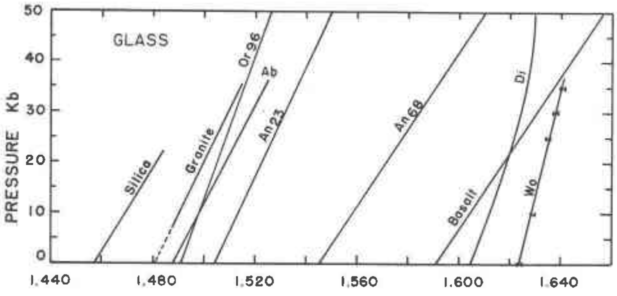

FIG. 4. Pressure-refractive index diagram, showing the change of refractive indices of glasses with pressures. The silica glass was heated to 675°–720°C, but all other glasses were quenched from runs just above the liquidus at high pressure. Wo = $CaSiO_3$ glass (present study); Di = diopside glass (Boyd and England, 1963); Basalt = basaltic glass (Cohen, Ito, and Kennedy, 1967); Ab = albite (Boyd and England, 1963); Granite = muscovite granite glass (Huang, 1973); Or_{96} = orthoclase glass; An_{23} and An_{68} = plagioclase glass (Chao and Bell, 1968); and Silica = silica glass (Cohen and Roy, 1965).

Figure 4 shows that the refractive index values for diopside and $CaSiO_3$ glasses vary as a function of pressure less than the values for glasses from feldspars, feldspathic rocks, and silica. The relatively small rates of increase in indices of refraction with pressure might suggest either that the rates of increase in densities of high-pressure diopside and $CaSiO_3$ liquids with pressure are small, or that the high-pressure liquid structures from inosilicates retain their densities less effectively than those from tektosilicates when quenched into glasses.

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References

BELL, P. M., AND H. K. MAO (1971) Subsolidus reactions of jadeite ($NaAlSi_2O_6$) and albite ($NaAlSi_3O_8$). *Carnegie Inst. Wash. Year Book*, **69**, 121–129.

BORG, I. Y., AND D. K. SMITH (1969) Calculated X-ray powder patterns for silicate minerals. *Geol. Soc. Am. Mem.* **122**, Boulder, Colorado.

BOYD, F. R., AND J. L. ENGLAND (1963) Effect of pressure on the melting of diopside, $CaMgSi_2O_6$, and albite, $NaAlSi_3O_8$, in the range up to 50 kilobars. *J. Geophys. Res.* **68**, 311–323.

———, ———, AND B. T. C. DAVIS (1964) Effects of pressure on the melting and polymorphism of enstatite, $MgSiO_3$. *J. Geophys. Res.* **69**, 2101–2109.

———, P. M. BELL, J. L. ENGLAND, AND M. C. GILBERT (1967) Pressure measurements in single-stage apparatus. *Carnegie Inst. Wash. Year Book*, **65**, 410–414.

CHAO, E. C. T., AND P. M. BELL (1968) Annealing characteristics of dense feldspar glass. *Carnegie Inst. Wash. Year Book*, **67**, 126–130.

CLARK, S. P. (1966) Handbook of Physical Constants, *Geol. Soc. Am. Mem.* **97**, New York, N. Y.

COHEN, H. M., AND R. ROY (1965) Densification of glass at very high pressure. *Phys. Chem. Glasses*, **6**, 149–160.

COHEN, L. H., K. ITO, AND G. C. KENNEDY (1967) Melting and phase relations in an anhydrous basalt to 40 kilobars. *Am. J. Sci.* **265**, 475–518.

ESSENE, E. (1974) High-pressure transition of $CaSiO_3$. *Contrib. Mineral. Petrol.* **45**, 247–250.

HUANG, W. L. (1973) *Water-Deficient Melting Relations of Muscovite–Granite, and Related Synthetic Systems to 35 Kilobars Pressure with Geological Applications.* Ph.D. Thesis, The University of Chicago, Chicago, Illinois.

———, AND P. J. WYLLIE (1974) Liquidus relationships between carbonates and silicates in parts of the system $CaO–MgO–SiO_2–CO_2–H_2O$ at 30 kb [abstr.]. *Trans. Am. Geophys. Union*, **55**, 479.

IRVING, A. J., AND P. J. WYLLIE (1975) Subsolidus and melting relationships for calcite, magnesite and the join $CaCO_3$–$MgCO_3$ to 36 kilobars. *Geochim. Cosmochim. Acta*, **39**, 35–53.

KNAPP, W. J., AND H. FLOOD (1961) Activities and structure of some borosilicate melts. *Geochim. Cosmochim. Acta,* **23**, 61–77.

KUSHIRO, I. (1964) Wollastonite-pseudowollastonite inversion. *Carnegie Inst. Wash. Year Book,* **63**, 83–84.

OSBORN, E. F., AND J. F. SCHAIRER (1941) The ternary system pseudowollastonite–akermanite–gehlenite. *Am. J. Sci.* **239**, 715–763.

RINGWOOD, A. E., AND A. MAJOR (1967) Some high-pressure transformations of geophysical importance. *Earth Planet. Sci. Lett.* **2**, 106–110.

ROBIE, R. A., AND D. R. WALDBAUM (1968) Thermodynamic properties of minerals and related substances at 298.15 K (25°C) and one atmosphere (1.013 bars) pressure and at higher temperatures. *U. S. Geol. Surv. Bull.* **1259,** 256 p.

TOMLINSON, J. W., M. S. R. HEINES, AND J. O. M. BOCHRIS (1958) The structure of liquid silicates, II. Molar volumes and expansivities. *Faraday Soc. Trans.* **54**, 1822–1833.

TRÖjer, F. J. (1968) The crystal structure of a high pressure polymorph of $CaSiO_3$. *Naturwissenschaften,* **55**, 442.

——— (1969) The crystal structure of a high pressure form of $CaSiO_3$. *Z. Kristallogr.* **130**, 185–206.

WILLIAMS, D. W., AND G. C. KENNEDY (1969) Melting curve of diopside to 50 kilobars. *J. Geophys. Res.* **74**, 4359–4366.

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