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HIGH PRESSURE STUDIES OF THE SYSTEM GeO_2-SiO_2

W. S. Miller, F. Dachille and R. Roy

January 30, 1963

University Park, Pennsylvania

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INTRODUCTION

In 1956, Shafer and Roy(1) reported some preliminary results of an isobaric study of the system GeO_2-SiO_2 as part of a series of investigations of analogs of silica, with special interest in the possibilities of solid solutions between isomorphs. A continued interest in this subject led to the present work, consisting chiefly of isothermal studies of the same system at high pressures. These observations were made on runs carried out in opposed anvil apparatus. In our earliest thinking on super-pressure calibration, it was proposed that a binary system with extent of solid solution changing with pressure would provide an excellent potential continuous calibrant. In addition, some of the hydrothermal runs of Shafer and Roy were repeated and new ones made in order to complete the p-t-x representation of the phase relationships existing in the system.

Preparation of Mixtures

Since the work cited above showed that simple mixing of silicic acid with germania quartz gave results identical with those obtained for mixtures prepared by simultaneous hydrolysis of the mixed tetrachlorides, all mixtures used in the later work were prepared from the hexagonal (quartz) form of GeO_2 and an amorphous SiO_2, mulled under alcohol, and dried. If the amorphous silica used in the first method was a precipitated silicic acid there was no detectable difference between results obtained with samples prepared by the two methods. However, when "Cab-o-Sil" was used as the source for the mix, it was sometimes found difficult to reach true equilibrium, especially in the hydrothermal runs.

Experimental

The opposed anvil devices used in this work have been described elsewhere(2). Steel anvils (speed star, HS66, or the equivalent) were used for runs under 45 kb. Anvils with tungsten carbide inserts were used for runs at higher pressures up to 130 kb at 325°C. Two series of experiments were carried out; one at 500°C and the other at 450°C, the latter being used to extend the upper pressure limits. In every case the products were temperature-quenched under pressure in the hope that all crystal forms present at the higher temperature might persist and be identified at room temperature. Idenfication was made by means of x-ray powder diffraction patterns obtained with a Norelco diffractometer. Microscopic examination also was carried out on certain samples, as described in the discussion of the results. Evidence for solid solutions was sought by carefully determining the value of 2θ for selected diffraction peaks for the phase found and comparing them with those of corresponding peaks on patterns obtained from the respective pure phases.

Those products which consisted of a single phase were used to establish a curve showing the variation with compositions of 2θ values for a particular reflection, e.g. quartz (112) (Fig. 1). This indicates a considerable departure from the ideal relationship. The curve then was used to determine the composition of the quartz solid solution phase in other products.

Results and Discussion

Figure 2 shows the phase boundaries for the system. With the exception of a small triangular coesite-quartz (ss) field, it may be noted that at these temperatures and at pressures under about 30 kb, the silica took the form of α-quartz with small amounts of germania in solid solution At higher germania concentrations where the amount of GeO_2 exceeded the solubility limit the remaining germania always was found to be in the rutile form, with no evidence of solid solution of SiO_2 in the phase. At pressures above 30 kb the silica appeared as coesite and the germania again was in the rutile form. In the small area previously referred to some of the silica was found as coesite and some in the quartz solid solution.

At 10,000 psi, in hydrothermal runs, the limit of solubility of germania in silica at 300°C is approximately 24% GeO_2, increasing slightly with temperatures to a maximum of about 31.5% at 750°C. (see Fig. 3, modified after Shafer and Roy$^{(1)}$). Thus the results of the hydrothermal runs are in general agreement with those of the anvil runs; it can be seen in Figure 2 that at lower pressures the curves approach the 25-26% region. This agreement between the results obtained with true hydrostatic pressures and the calculated anvil pressures argues for the correctness of the latter. As the pressure increases, solid solution in the quartz-rutile field decreases until (at the upper temperature limit of this study) at 31.5 kb the silica inverts to the dense form, coesite and no longer accepts measurable amounts of germania. However, solid solution increases with pressure in the qz-coesite field until the boundary intersects with that of the qz-rutile field at the eutectic pressure.

At these higher pressures (above 31.5 kb at 500°C, or above 27.5 kb at 450°C) coesite is unmistakably present in mixtures containing less than 50% GeO_2. At higher concentrations the x-ray patterns are dominated by that of the rutile phase. Since coesite diffraction peaks no longer are clearly present beyond this point, it was thought that the silica was dissolving in the GeO_2-rutile. (Stishovite, the very dense form of silica, has a rutile structure$^{(3)}$. However, careful measurement of the GeO_2-rutile x-ray diffraction spacings gave no evidence of solid solution. It is not yet known whether failure of the silica to assume the rutile structure in crystalline solution with germania under the conditions of the present experiments is real or due to a kinetic barrier, or to inability to "quench" a highly metastable solid solution. Although no detailed attempt was made to study the ternary system GeO_2-SiO_2-H_2O there is evidence of the very marked effect of water content on liquidus temperatures at certain pressures. Two 50 mole percent mixtures (with about 10% H_2O) quenched to a glass after 40 hours at 911°C and 0.67 kb while a similar run made with excess water as "mineralizer" quenched to crystal phases. Also three 10 mole percent GeO_2 mixture (with about 15% H_2O) set up in the opposed anvil apparatus at 4 kb at 500 and 596°C apparently produced glasses in less than 2 hours at these conditions. When the pressure on the glasses was raised to 19 kb and held for 24 hours they failed to crystallize at 500°C. Identical runs made without the heating period at 4 kb yielded the qz (ss) phase.

The possibility exists that a melt is formed at certain p-t conditions passed through as the samples are brought to selected higher values where crystallization of GeO_2 (rutile) takes place rapidly while silica remains in the amorphous phase, only very slowly crystallizing as coesite.

Microscopic examination did reveal numerous amorphous grains edged or coated with micron-sized crystals of GeO_2

rutile. These grains, found in the products of 50 and 80 mole percent mixtures had refractive indices between 1.560 and 1593. In the case of the 80 mole percent products a gravity separation was used to concentrate the silica fraction which showed more clearly the presence of amorphous and coesite grains. The high refractive indices of the glass grains of their general composition range are in keeping with the findings of Cohen and Roy(4) on the densification of glasses under pressures. They show that silica glass and germania densified at conditions similar to the present ones have refractive indices of 1.53 and 1.67 approximately, increased from 1.458 and 1.608 respectively.

Attempts to overcome the sluggish nature of the reactions by the use of displacive shearing stresses were not successful. The silica end member, 30 and 50 mole percent compositions subjected to pressures in excess of 100 kb under shearing conditions(5) at 400-450°C for 2.5 to 22 hours gave no satisfactory x-ray or microscopic evidence of the formations of stishovite, rutile phase or coesite phase solid solutions.

That the failure to obtain a rutile structure phase may be a matter of kinetics is strongly suggested also in the results of a related study with the excellent "weakened" SiO_2 model, BeF_2. It has been observed that the crystallization of the quartz and coesite phases of BeF_2 from glass proceeds under appropriate pressures at very much greater rates than for the SiO_2. Furthermore, the transition of BeF_2 quartz to coesite(2) which takes place essentially at the same p-t conditions as for the corresponding SiO_2 transition also proceeds at a much higher rate. It appeared reasonable to expect the formation of a rutile phase of BeF_2 at pressures above those reported in the synthesis of stishovite (initially about 110 kb, now down to about 80 kb(5,6) because of the greater ease of solid state transition reactions with this compound. However, the following runs at pressures from 100-160 kb failed to produce a rutile phase of BeF_2:

160 kb	250°C	10 hrs.	BeF_2 qz. remained qz.
160 kb	325°C	14 hrs.	BeF_2 qz→qz + coesite
100 kb	340°C	2 hrs.	BeF_2 glass → coesite

It should be noted that even with BeF_2 the solid state reactions become very sluggish at lower temperatures.

Microscopic examinations were carried out in a further search for the silica. In the samples prepared at pressures above 30 kb and at concentrations higher than 50% GeO_2 grains of coesite could be observed. Whether the amount of coesite accounts for all the silica, and why it does not appear on the x-ray patterns are questions not yet answered. It may be possible that the silica does dissolve in the germania at high pressures but the solid solution is not stable when the pressure is dropped, breaking down into pure germania rutile and amorphous silica not observable by the usual means. However, the intervention of a glass phase with subsequent sluggish devitrification may be a likely mechanism. All that can be said at present is that a quenchable GeO_2-SiO_2 rutile solid solution does not appear to exist under the conditions of the investigation, although SiO_2 can assume the rutile structure if the pressure is high enough.

Acknowledgement

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Table 1

Uniaxial Anvil Runs: 450°C

Mole % GeO_2	Pressure	Time	Phases
5.0	13 kb	24 hours	quartz (ss)
5.0	25 "	20 "	quartz (ss), minor coesite
5.0	30 "	23 "	quartz (ss), coesite
5.0	50 "	40 "	coesite
5.0	70 "	42 "	coesite, minor rutile
17.5	13 "	24 "	quartz (ss), minor rutile
17.5	25 "	30 "	rutile quartz (ss)
17.5	30 "	24 "	rutile, minor qz (ss), minor coesite
17.5	50 "	24 "	coesite, rutile
17.5	70 "	24 "	coesite, rutile
30.0	13 "	24 "	rutile, quartz (ss)
30.0	30 "	24 "	rutile, quartz (ss), tr. coesite
30.0	50 "	24 "	rutile, minor coesite
30.0	70 "	24 "	rutile, minor coesite
37.5	13 "	24 "	rutile, quartz (ss)
37.5	30 "	24 "	rutile, minor qz (ss), tr. coesite
37.5	50 "	24 "	rutile, minor coesite
37.5	70 "	24 "	rutile, minor coesite
50.0	13 "	24 "	rutile, quartz (ss)
50.0	30 "	24 "	rutile, minor quartz (ss)
50.0	50 "	24 "	rutile, trace coesite
50.0	70 "	48 "	rutile, trace coesite
50.0	80 "	40 "	rutile, minor coesite
70.0	80 "	24 "	rutile, trace coesite
80.0	13 "	21 "	rutile, minor qz (ss)
80.0	30 "	24 "	rutile, minor qz (ss)
80.0	50 "	39 "	rutile, trace coesite
80.0	70 "	40 "	rutile, trace coesite

Table 2

Uniaxial Anvil Runs: 500°C

Mole % GeO_2	Pressure	Time	Phase
5.0 %	11 kb	42 hrs.	quartz (ss)
5.0	20 kb	39 "	quartz (ss)
5.0	21.5 kb	42 "	quartz, coesite
5.0	23 kb	46 "	quartz, coesite
5.0	48 kb	25 "	coesite, rutile*
11.0	24.5 kb	42 "	quartz (ss)
11.0	30 kb	64 "	coesite, trace quartz (ss)
11.0	33.5 kb	38 "	coesite, rutile
11.0	52 kb	22 "	rutile, coesite
16.0	22 kb	36 "	quartz (ss), trace rutile
16.0	30 kb	24 "	quartz (ss), minor rutile
22.5	10 kb	40 "	quartz (ss), trace rutile
22.5	11 kb	40 "	quartz (ss), minor rutile
22.5	30 kb	24 "	quartz (ss), rutile
29.0	30 kb	64 "	rutile, coesite, quartz (ss)
29.0	31.5 kb	55 "	rutile, coesite
29.0	32 kb	37 "	coesite, rutile
29.0	54 kb	22 "	coesite, rutile
75.0	29 kb	47 "	rutile, quartz (ss)
75.0	32 kb	50 "	rutile, coesite

*Rutile refers to GeO_2, rutile form

Table 3

Miscellaneous Anvil Runs

Mole % GeO_2	Pressure	Temperature	Time	Phase
10%	110 kb	400°C	26 hrs.	coesite, minor rutile
50%	50 kb + shear	450°C	16 hrs.	rutile quartz (ss)
50%	55 kb + shear	450°C	22 hrs.	rutile, tr. coesite
50%: glass from 904°C Ht-run	90 kb	450°C		rutile, coesite
0: (all SiO_2)	100 kb + shear	400°C	2.5 hrs.	coesite
50%	110 kb + shear	400°C	3.25 hrs.	rutile, tr. coesite

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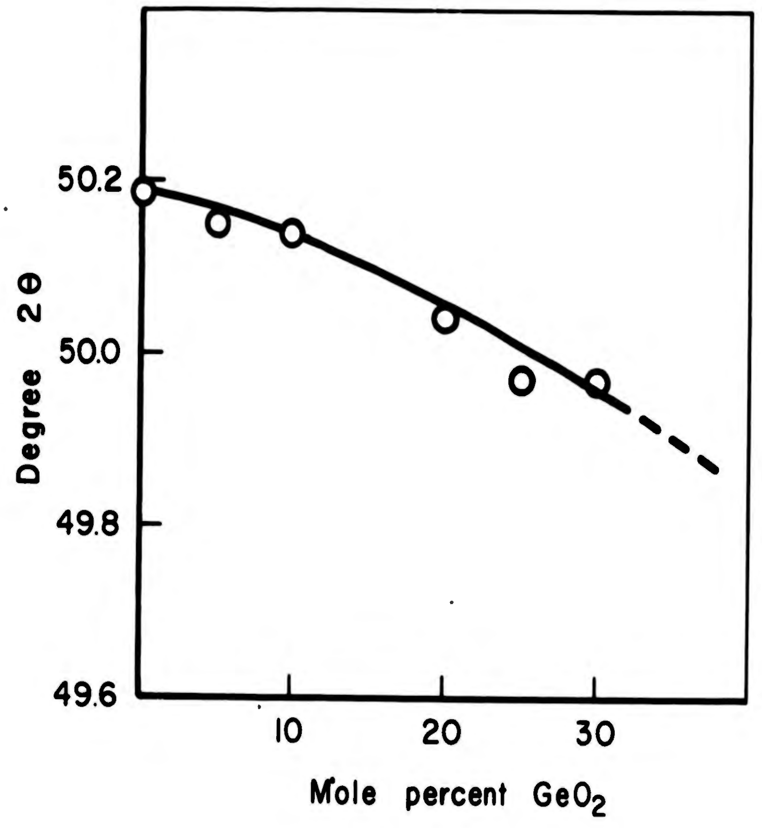

Figure 1. Change of the quartz solid solution (112) in terms of two theta of copper K alpha radiation

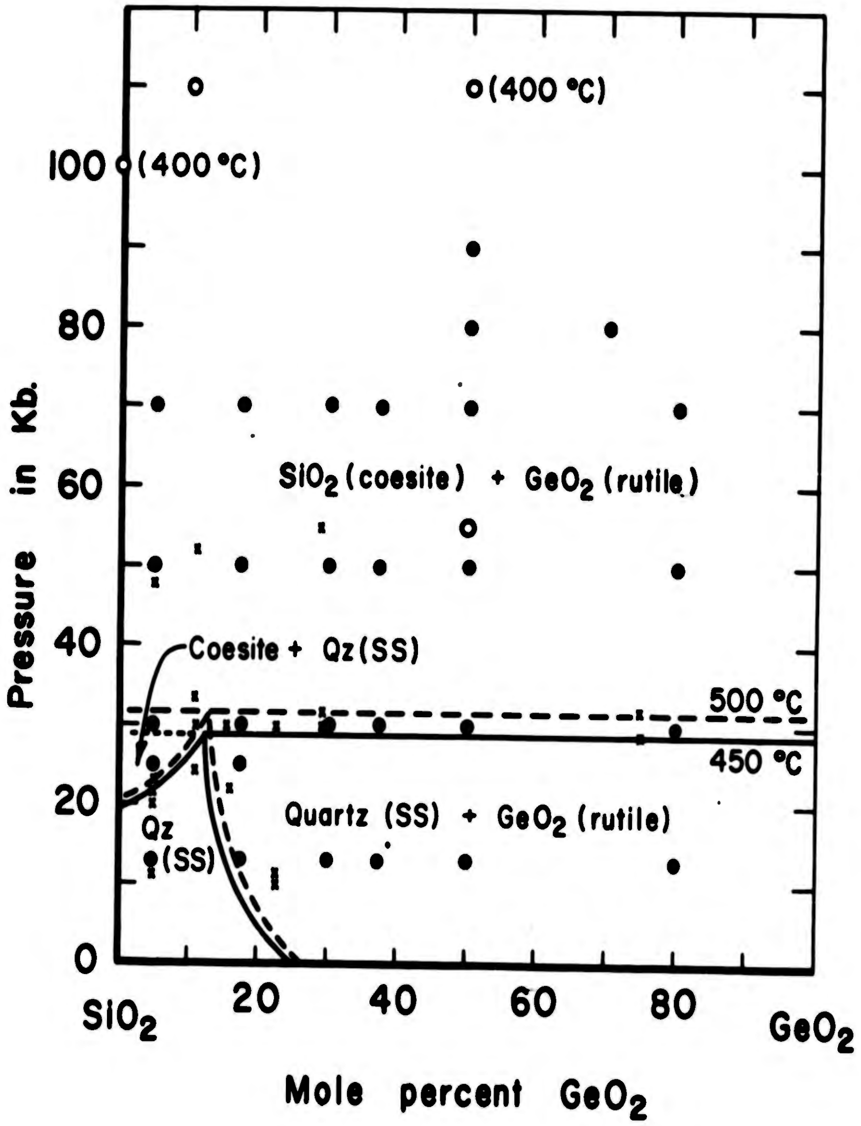

Figure 2. Isothermal studies of the system SiO_2-GeO_2 in opposed anvil apparatus. Data at 450 degree C is plotted as dots; at 500 degrees as Xs; a few at 400 degrees as open circles.

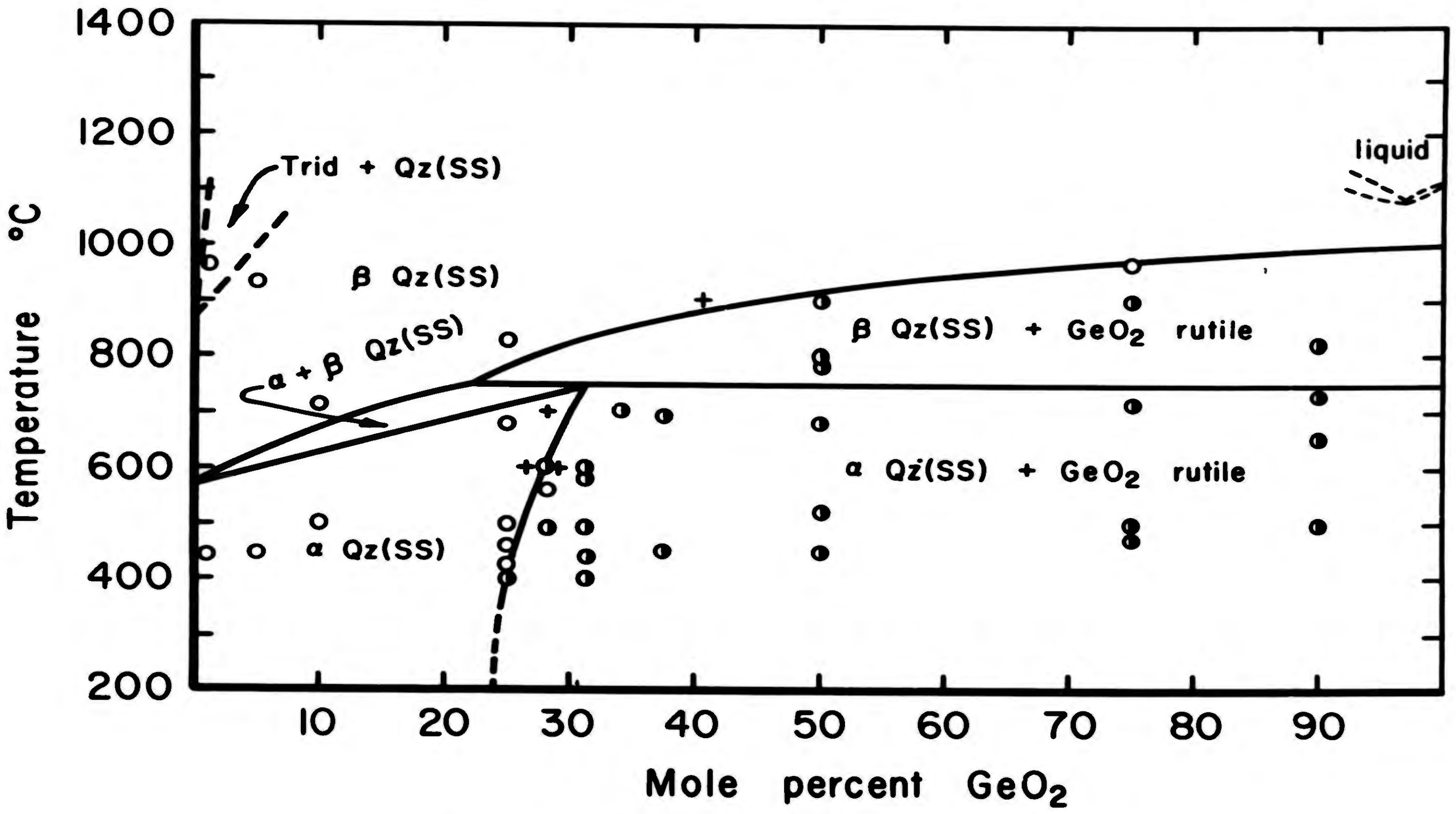

Figure 3. Phase diagram of the system SiO_2-GeO_2 based on studies under dry conditions, and under hydrothermal conditions at 10,000 psi.

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