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QUARTZ-COESITE STABILITY RELATIONS AT HIGH TEMPERATURES AND PRESSURES*

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ABSTRACT. Coesite-quartz stability relations have been investigated using the "simple squeezer" high-pressure apparatus. Samples of amorphous SiO_2 in the form of silicic acid ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) were subjected to pressures up to 80,000 bars and temperatures from 400-800°C. The equation of the curve separating the fields of quartz and coesite is $P = 22.5 T + 9500$ where P is in bars and T is in degrees Centigrade with coesite stable in the high-pressure region. The only phases produced were quartz and coesite. The equilibrium curve plus estimated thermal gradient in the Earth indicate that quartz should invert to coesite at a depth between 60 and 100 kilometers within the Earth.

The entropy of coesite at 25°C and one bar is 8.6 ± 0.7 cal/deg.mole as determined by the equilibrium curve. The heat of transition of quartz to coesite is -225 ± 150 cal/mole. The thermal data on coesite indicate that the approximate maximum depths within the Earth at which fayalite and forsterite are stable relative to "FeO" and MgO plus coesite are 200 and 1100 km.

INTRODUCTION

Coes (1953), in the first announcement of the very important high-pressure work carried on at the Norton Company, Worcester, Massachusetts, describes the synthesis of a new high-pressure polymorph of SiO_2 . The new polymorph is characterized by a density of 3.01, 13.6 percent denser than quartz. Sosman (1954) proposed that the new polymorph be called coesite. Since this polymorph has not as yet been found in nature, Sosman also suggested the alternative name "Silica C." In the present paper the new polymorph will be called coesite.

Coes synthesized coesite at pressures near 35,000 bars in the temperature range 500-800°C from various mixes. At temperatures above 800°C and at about 35,000 bars quartz formed from the mixes rather than coesite. This result was then the first indication of the position of the equilibrium curve between coesite and quartz. Griggs, Kennedy, and Fyfe (1955) in the course of investigating various reactions at high pressures, synthesized coesite at lower pressure and temperatures than those reported by Coes. Because of the geologic importance of quartz, it was thought desirable to obtain in greater detail the equilibrium curve between coesite and quartz. This curve would fix the maximum pressures at which quartz could form and, together with the temperature gradient in the Earth, would fix the maximum depth within the Earth at which quartz would be stable.

The problem of the quartz-coesite equilibrium is part of the more general problem of the stability of minerals having a loosely packed framework structure. Minerals with such framework structures (feldspars, feldspathoids,

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quartz, etc.) make up a major portion of the rocks exposed at or near the Earth's surface. An important question is: to what maximum depth within the Earth are such minerals stable? It appears very probable that high density phases having compositions of these framework minerals are stable at moderate depths within the Earth. Robertson, Birch, and MacDonald (in press) have shown that nepheline plus albite might be expected to convert to the denser phase, jadeite, at depths of approximately 10 to 40 km within the Earth. Pure albite would invert to jadeite plus quartz at somewhat greater depths. Since alkali feldspar plus quartz are the dominant constituents of granites and granodiorites, it might be possible to have a rock equivalent in composition to a granite, but made up of denser, less compressible phases at a moderate depth within the Earth. The depth at which such a rock would be stable would depend on the position of the quartz-coesite equilibrium curve as well as on the position of the breakdown curves for the alkali feldspars, and of the temperature gradient.

The present study is concerned with the direct experimental determination of the quartz-coesite equilibrium relations. Silicic acid ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) and quartz have been converted to coesite at high pressures. From the position of the equilibrium curve and the thermodynamic properties of quartz, approximate thermodynamic properties of coesite have been obtained. These properties allow an estimate of the upper pressure limit of stability of such minerals as olivine and pyroxene, long considered the dominant constituents of the Earth's mantle.

EXPERIMENTAL DETAILS

The experimental work was carried out on the "simple squeezer" high-pressure apparatus designed by Professors Griggs and Kennedy and described by Griggs, Kennedy, and Fyfe (1955). Since this high-pressure system is being described in detail by Griggs and Kennedy elsewhere, only the basic features of the apparatus need be mentioned here. The confining pressure is produced by pressing two pistons together. The piston faces that come in contact across the specimen have a diameter of $\frac{1}{4}$ inch. The sample is placed between the piston faces and is separated from each face by a layer of platinum-10% rhodium foil. The pistons are pressed together by a commercial hydraulic jack, supported by a framework of plates and tie rods. The sample is heated by an external furnace enclosing the pistons and sample. The temperature is measured by a chromel-alumel thermocouple placed in a hole in one of the pistons. The tip of the thermocouple is about $\frac{1}{4}$ inch from the sample.

In the simple squeezer the pressure is not directly measured but is calculated from the force applied to the confining pistons. The sample between the pistons may not be under a hydrostatic pressure, and the strain energy resulting from shearing the sample might affect the position of the equilibrium curve. There is an uncertainty in the pressure acting on the sample and an uncertainty in the effect of shear on equilibrium relations. An attempt to evaluate these uncertainties has been made (MacDonald, in press). The calcite-aragonite equilibrium curve was determined, using the simple squeezer,

and the results were compared with those of Jamieson (1953) derived from thermochemical considerations. The simple squeezer gave an equilibrium curve about 1500 bars lower in pressure at 10,000 bars than the curve obtained by Jamieson. The reasons for this discrepancy are as yet uncertain but they do indicate perhaps that pressures calculated for the simple squeezer may be uncertain by as much as 15 percent.

The starting material in all but a few exploratory runs was Mallinckrodt silicic acid, $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. Various other materials were tried but none gave as good reaction times as $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. As an illustration of this, quartz at 580° and 30,000 bars showed about 10 percent conversion to coesite in a one-hour run. Silicic acid showed 100 percent conversion to coesite. Various mixtures of alkali silicates were also tried but not used because of the appearance of phases other than quartz and coesite. Using $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, the only phases observed either optically or by X-ray were quartz and coesite.

The products were identified by comparing the X-ray patterns obtained on a Norelco high angle diffractometer with a standard quartz pattern and with the X-ray spacings of coesite given by Coes (1953). The pattern of coesite is quite distinctive, and there is no chance of confusing the pattern with that of other phases of SiO_2 . The products were also examined optically. Since coesite has a mean index of refraction of 1.60, it is readily distinguishable from quartz, and small amounts of coesite can be detected.

The sample to be exposed to high pressures is placed on the platinum-10% rhodium foil in the form of a dry powder or admixed with a drop of water to form a paste. The presence of water does not appear to affect either the position of the equilibrium curve or the rate at which equilibrium is attained. An original thickness of powder of 0.02-0.03 inch results in a wafer about .005 inch thick in the center. The wafer is generally transparent, though in some cases milky in appearance.

The sample is first heated to the desired temperature and then the pressure is raised. The time required to bring the sample to temperature varied from 15 to 30 minutes. The application of pressure took only a few seconds. The order of raising the temperature and pressure is important. By first raising the temperature and then the pressure, the sample is at a high pressure only at the desired temperature. The high-pressure form, coesite, can form only at the required temperature and not at some lower temperature. After the sample is held at the required conditions of temperature and pressure for a suitable time, ranging from one to 24 hours, depending on the conditions of the experiment, the sample is quenched by releasing the pressure and placing the sample in water. In this way temperature and pressure are reduced to room values in about 5 seconds. This quenching assures that coesite formed at high pressures is not converted to quartz in the process of cooling the sample.

RESULTS

The results of 43 runs are summarized in table 1. This table lists the temperature and pressure conditions of the experiment and results from X-ray

and optical examination of the products. Almost all the runs were made in the temperature range 400-600°C. The lower limit in temperature was set by the rate of reaction. At 350°C runs of 24 hours did not produce coesite even though the runs were well inside the coesite field. At 400°C coesite formed in 24 hours or less. The upper limit in temperature of 600°C was set by the use of high-speed steel pistons. These pistons do not deform appreciably at temperatures below 600°C and pressures below 30,000 bars but do deform rapidly at higher temperatures. One important run at 815° and 31,000 bars was made using Kentanium pistons. This experiment, as well as three other runs at pressures about 50,000 bars, were made in collaboration with Professor David T. Griggs.

The length of time the sample was held at the required temperature and pressure depended on the temperature of the run. The runs at 400°C were maintained at temperature and pressure for 10-24 hours, whereas runs near 600°C were only about an hour in duration. In this fashion an attempt was made to achieve at least partial equilibrium at all temperatures. Repeat runs of increased duration were made near the boundary curve. A run at 480°C and 20,000 bars for one hour produced only quartz. Since this run is near the boundary, it was repeated and held at pressure for 20 hours. The longer run again produced only quartz. Similarly, runs of one hour at 500°C and 22,000 bars produced coesite, while an 8-hour run at 500°C and 20,000 bars produced only quartz.

The points that were used to determine the equilibrium curve are shown in figure 1. Only those points near the curve are plotted. The solid black squares indicate runs in which coesite was formed. Strictly speaking, the boundary line is a line separating runs in which a small amount of coesite formed from runs in which no coesite formed at all. The results of the runs are consistent, and repeat runs of longer duration do not alter this boundary. For these reasons the boundary curve is thought to represent the equilibrium curve. In order to demonstrate that this curve is actually the equilibrium curve, a detailed study should be made using coesite as a starting material and showing that coesite converts to quartz at pressures lower than those given by the curve in figure 1. In the present study insufficient coesite was made to carry out such a program.

The size of the squares in figure 1 is approximately proportional to the estimated uncertainty in the conditions of the individual run. The uncertainty in temperature is estimated to be about $\pm 10^\circ\text{C}$, due to the difficulty in placing the thermocouple in the identical position relative to the sample in every run. The pressure uncertainty in any given run is estimated to be ± 500 bars, due to the scale of the pressure gauge on the jack and small changes in pressure during a run resulting from fluctuations in room temperature. This estimate of the uncertainty assumes that the total force acting on the piston gives a good measure of the pressure and that in addition the pressure is uniform over the entire sample.

The equation representing the equilibrium line is $P = 22.5(\pm 8) T + 9500(\pm 4000)$, where T is in degrees Centigrade and P is in bars. The estimated uncertainties are derived by examining possible curves that could be

TABLE I
Results of Subjecting $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ to High Temperatures and Pressures

Temperature °C	Pressure bars	Time hrs	Results of X-ray and optical examination of materials
382	62,000	1.5	coesite
390	83,000	1.5	coesite
396	28,000	16	coesite and minor quartz
400	17,500	22	quartz
408	19,500	14	minor coesite and quartz
414	18,000	10	quartz
432	16,000	13	quartz
440	18,000	2	quartz
440	18,000	11	quartz
442	20,000	12	quartz
454	18,000	1	coesite and quartz
475	21,000	1	quartz
480	20,000	1	quartz
480	20,000	2	quartz
485	56,000	20	quartz
490	18,000	1	coesite
492	16,000	1	quartz
493	16,000	1	quartz
500	19,000	24	quartz
500	20,000	18	quartz
500	20,000	2	quartz
500	20,000	8	quartz
500	22,000	1	quartz
500	23,000	1	minor coesite and quartz
500	30,000	1	coesite and quartz
504	19,000	10	coesite
524	21,000	2	quartz
530	24,000	1	minor coesite and quartz
536	22,000	1	coesite and quartz
540	22,000	1	quartz
540	22,000	1	quartz
540	23,000	1	quartz
550	19,000	1	minor coesite and quartz
550	20,000	1	quartz
550	21,000	1	quartz
554	25,000	6	quartz
560	23,000	4	coesite and quartz
573	24,000	1	minor coesite and quartz
576	23,000	1	coesite and quartz
580	22,000	1	quartz
580	30,000	6	quartz
582	22,000	1	coesite
584	26,000	1	quartz
590	24,000	1	coesite and quartz
815	31,000	1	minor coesite and quartz
		1	minor coesite and quartz

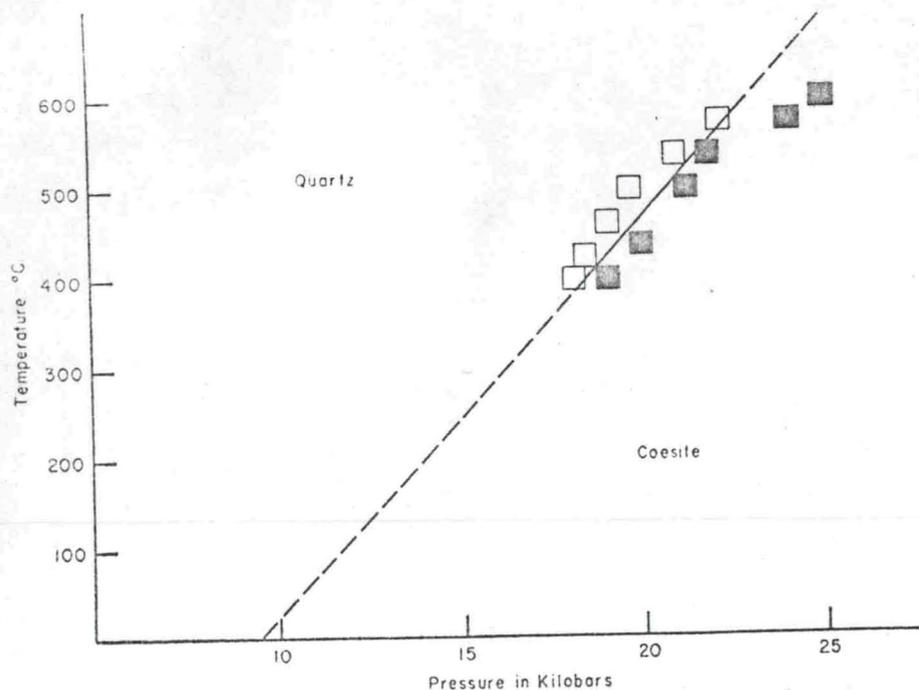


Fig. 1. Plot of runs used in determining quartz-coesite equilibrium curve. Size of square is approximately proportional to estimated uncertainty in the temperature and pressure of the run. One square may represent two or more runs. (See table 1.)

drawn without contradicting the experimental determinations, taking into account the uncertainty in the individual points. The major reason for the large uncertainties is that the temperature interval in which the reaction has been studied is only 200°C. The run at 815°C and 31,000 bars reduced this uncertainty somewhat, but more measurements are needed at high temperatures and pressures.

OTHER POSSIBLE HIGH-PRESSURE POLYMORPHS OF SiO₂

Three runs were made at pressures greater than 50,000 bars in order to investigate possible higher-pressure forms of SiO₂. A run at about 83,000 bars and 390°C produced only coesite. The run was only an hour and a half long, so that equilibrium may not have been reached at this low a temperature. It is considered very probable that a series of higher density forms of SiO₂ can be synthesized. It is most improbable that coesite is the form of SiO₂ having a rutile type of structure with silicon in six coordination, as suggested by Thompson (Birch, 1952, p. 234). Such a form should have a density of roughly 4.5 to 5.0. Since coesite has a density of only 3.0, a number of intermediate forms of SiO₂ are possible before a rutile-like form of SiO₂ is reached at extreme pressures.

THERMODYNAMIC DATA ON COESITE

The slope of the curve of univariant equilibrium shown in figure 1 and the intersection of the curve with the zero pressure axis, together with thermodynamic data on quartz, allow an estimate of the entropy and heat of formation of coesite. The slope of the curve determines the entropy of coesite, provided the difference in volume between coesite and quartz is known, since $dP/dT = \frac{\Delta S}{\Delta V}$. The density of coesite is 3.01 as reported by Coes (1953) and Ramsdell (1955). Using this density and the density of quartz, the volume change for the transition



is given by $\Delta V = -2.71 \pm 0.1$ cc/mole. The determined slope of the curve is 22.5 ± 8 bars/degree, which leads to a value of the change in entropy for the transition of $\Delta S = -1.4 \pm 0.6$ cal/deg.mole. Since quartz has an entropy at 25°C and 1 bar of 10.0 cal/deg.mole (Kelley, 1950), coesite has an entropy of 8.6 ± 0.7 cal/deg.mole at 25°C and 1 bar. In this calculation of the entropy it is assumed that the difference in compressibility of quartz and coesite is less than 1×10^{-5} bars⁻¹ and that the difference in thermal expansion is less than 1×10^{-4} degrees⁻¹, since the entropy change is strictly valid only at 10,000 bars and should be corrected for the change of entropy with pressure. This change is probably considerably smaller than the uncertainties introduced by the uncertainty in slope of the transition curve. Furthermore it is assumed that the transition curve is a straight line, since the experiments are not of sufficient accuracy to detect any curvature.

The heat of transition for the reaction at 25°C and 1 bar is determined by the intersection of the transition curve with the 25° axis, provided that ΔV for the reaction is assumed constant, and the change of entropy for the reaction is known. Using an entropy change of -1.4 ± 0.6 cal/deg.mole and an intersection of $10,000 \pm 4000$ bars, a heat of transition of -225 ± 150 cal/mole is obtained.

TABLE 2
Thermochemical Data on Quartz and Coesite

	V cc/mole	S cal/deg.mole	ΔH_f cal/mole
quartz	22.64	10.0 ± 0.1	0
coesite	19.93 ± 0.1	8.6 ± 0.7	-225 ± 150

POSSIBLE NATURAL COESITE

Coesite has not as yet been found in nature. The stability curve and estimated temperature gradients within the Earth (Birch, 1955) indicate that quartz should convert to coesite at a depth between 60 and 100 kilometers within the Earth. This indicates that any rock containing excess SiO₂ and originating at 100 km within the Earth should contain coesite, provided the rock had not subsequently undergone thermal metamorphism. In addition, the quartz-coesite boundary lies some 20 to 30 km above the graphite-diamond

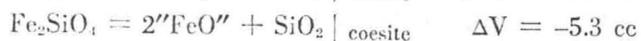
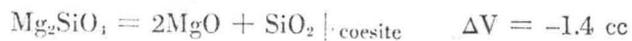
transition boundary within the Earth (MacDonald, ms.), so that any rock in which diamonds crystallized should contain coesite, provided the rock were oversaturated with respect to SiO_2 . The eclogite inclusions found within the kimberlite pipes of South Africa might contain coesite, since they contain diamonds, but most of the eclogites are undersaturated with respect to SiO_2 .

A preliminary search of thin sections of eclogite samples from South Africa, Austria, and Norway has disclosed no coesite. The search for coesite in rocks is made difficult by the fact that the optical properties of coesite are nearly identical with those of apatite.¹

O. F. Tuttle, at the New Orleans meeting of the Geological Society, made the very interesting suggestion that lamellae found in quartz grains in strongly deformed rocks might represent planes along which quartz has converted to coesite. The lamellae could then be interpreted in terms of a shear transformation in which the sheared region contains a new phase, coesite, and the boundary of the lamellae with the quartz is a phase boundary. The quartz lamellae are a possible natural source of coesite that should be investigated.

COESITE AND THE STABILITY OF OLIVINES AND PYROXENES AT DEPTH

The thermochemical data on coesite can be used to obtain a rough estimate of the maximum depth within the Earth at which these minerals are stable. Transitions of the form



show a negative volume change, since the mixture of the oxide and coesite has a lower volume than the corresponding olivine. At some high pressure the mixture of the oxides should become stable relative to the olivine, provided that no intervening high-pressure forms of olivine occur. Using the data on coesite and thermochemical data on the olivines and oxides (MacDonald, ms.), it is found that forsterite would break down to the oxides at a pressure of about 450,000 bars, while fayalite would break down at about 60,000 bars,² assuming the temperature to be on the order of 1000-2000°C. These conditions would correspond to a range of depths of 200-1100 km within the Earth. The mineral olivine is then probably unstable relative to the oxides at depths in the Earth below 1100 km. These calculations assume that no new phase of olivine appears with a density less than the density of the oxides and coesite, and

¹ Professor Harold Fairbairn has looked for coesite in eclogite. He reports: "An attempt to find coesite in an eclogite inclusion in kimberlite (Roberts Victor Mine, Transvaal) was unsuccessful. A 340 gm sample was separated into sized fractions. A -400 screen fraction weighing 80 gm was decomposed by HF, and heated successively in HCl and H_2SO_4 . The small remaining residue all floated in bromoform ($D = 2.9$), indicating no coesite ($D = 3.01$). Coarser fractions were treated with heavy liquids and passed through a Frantz separator. A small non-magnetic residue of density between 2.9 and 3.1 likewise failed to show any coesite."

² A single experiment was made to test this conclusion in which synthetic fayalite provided by Professor Kennedy was held at 480°C and 56,000 bars for one hour. No change was observed in the fayalite. The experiment is not considered conclusive since the run was only one hour long and equilibrium may not have been attained at this low temperature.

furthermore that no denser phases of FeO, MgO, and SiO_2 appear. The limits proposed above are then maximum limits; the appearance of still denser forms would lower the pressure needed to transform olivine. Similar calculations on pyroxenes indicate that the pyroxenes would also break down at comparable depths. The calculations are very approximate because of the high temperatures and pressures involved and the uncertainty of the compressibility and thermal expansion of the phases under these conditions. It is of interest to note that the range from 200 to 1100 km within the Earth includes the region (200-900 km) suggested by Birch (1952) as a region in which there is a gradual shift toward high-pressure modification of ferromagnesian silicates.

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