Problems of pressure estimation in high temperature experiments using solid media apparatus; pressure calibration with reference to breakdown of albite and quartz-coesite transformation (Part II)

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Abstract. The high albite (Ab) $\rightleftharpoons$ jadeite (Jd) + quartz (Q) reaction (1) and the quartz (Q) $\rightleftharpoons$ coesite (Cs) transformation (2) have been determined within the temperature range of 1000–1100°C and 1000–1400°C respectively under variable pressures using an anvil-with-hole apparatus. The equilibrium curves for the two reactions as a function of P and T are as follows:

$P = -1.33 + 0.0296 T$ (reaction 1); $P = 18.949 + 0.0111 T$ (reaction 2). These two lines intersect at 31.1 ± 0.5 kb and 1096°C. The possibility of using an anvil-with-hole apparatus for conducting current investigations is discussed in this paper.

Keywords. Pressure calibration; albite; quartz-coesite.

1. Introduction

Careful pressure-temperature calibration is very important in the study of phase equilibria as it is the only way to correlate data obtained from different laboratories with the help of solid media apparatus. The equilibria $Ab = Jd + Q$ and $Q = Cs$ are often used for this purpose. The precise absolute values of P – T parameters of these equilibria are unknown, though there have been multiple attempts to determine them.

Hays and Bell (1973) studied the analbite breakdown reaction in a gas apparatus at 600°C. It was found that at 16.2 ± 0.3 kb the reaction proceeds with albite growth but at 16.7 ± 0.3 kb this reaction is reversed, i.e. the equilibrium pressure is 16.45 ± 0.55 kb. Determination of equilibrium pressure in the piston cylinder apparatus at 600°C (which was carried out by workers from six different laboratories) has also revealed considerable deviations from this point (15.7–16.8 kb) for runs at relatively low pressures. Incidentally, the data on the salt cell (NaCl; 16.2 ± 0.5 kb; Johannes *et al* 1971) could be compared with precise hydrostatic determination. The higher accuracy of pressure measurements at a given equilibrium at 600°C using salt cells (as compared to talc and pyrophyllite ones) has been proposed experimentally (Johannes 1978).

Holland (1980) studied this reaction within the temperature range of 600–1200°C using the salt cell and proposed the following equation for the equilibrium line:

$$P = 0.35 + 0.0265 \pm 0.5 \text{ (kb)}$$
$$(16.25 \pm 0.25 \text{ kb at } 600^\circ\text{C}).$$

Mirwald and Massone (1980) also used the salt cell for pressure equilibrium

measurements at 1090°C and obtained the value of equilibrium pressure within the range of 31.0 ± 0.2 up to 31.7 ± 0.2 kb which essentially differed from Holland's (1980) data ($29.0 \pm 0.2 - 30.0 \pm 0.2$ kb).

It is obvious that the data obtained at relatively low temperatures (600°C) using the salt cell are in good agreement with the hydrostatic experimental data. However, at high temperatures (1000°C), there is a discrepancy in the pressure measurement related to albite breakdown line. The same is true for the $Q = Cs$ equilibrium. Salt cells (NaCl) were used three times during the study of this equilibrium. The equilibrium pressures for the last reaction were 29.5 ± 0.2 kb (Bohlen and Boettcher 1982), 30.5 ± 0.2 kb (Mirwald and Massonne 1980) and 31.2 ± 0.2 kb (Akella 1979) at 1000°C. It should be noted that the slopes (dP/dT) of equilibrium lines differ markedly from one another, hence the discrepancy in pressure estimation should increase with temperature. The discrepancies have prompted many research workers to study these equilibria accurately.

2. Starting material and research methods

The $Q \rightleftharpoons Cs$ transformation was studied using synthetic α -quartz (99.99% SiO_2). Coesite was synthesized from quartz. To study the high albite breakdown reaction, quartz, albite and jadeite were mixed in a molar ratio of 1:1:1. High albite and jadeite were synthesized from gel mixture at temperatures decreasing from 1000°C to 700°C at 6–10°C/s between 18 and 40 kb respectively. The run products were identified by X-ray diffraction. Reflections (100, 101); (002) and (310, 311) of quartz, albite and jadeite, respectively, were used to determine the direction of the high albite breakdown reaction. The changes of intensities at peaks less than 15% were taken as 'no reaction'. The starting material was loaded in carefully-sealed platinum capsules, the diameter of which was 3 mm. When the two-capsule technique was applied, they were in the form of hemispheres (refer part 1).

3. Results

The experimental results obtained are shown in figure 1 and tables 1 and 2. The following equations for the equilibrium lines were calculated by the least square method:

$$P(kb) = -1.33 + 0.0296 T^{\circ}C (Ab \rightleftharpoons Jd + Q),$$

$$P(kb) = 18.949 + 0.0111 T^{\circ}C (Q \rightleftharpoons Cs),$$

$$P(kb) = 16.70 + 0.013 T^{\circ}C (Ab \rightleftharpoons Jd + Cs).$$

In order to calculate the $Ab = Jd + Q$ equilibrium boundary, the data of Hays and Bell (1973) obtained at 600°C were taken into account. For pressure calculation, the breakdown of Ab to Jd + Q at 1160°C and to the intersection point of the $Ab = Jd + Q$ and $Q = Cs$ equilibrium curves were considered. The $P-T$ condition for the intersection point related to these two lines is 31.1 ± 0.5 kb and $T^{\circ}C = 1096 \pm 10$. The previous data on $Q = Cs$ transformation (Ishbulatov 1977) differ markedly from

Figure 1. P - T brackets on the $\text{Ab} \rightleftharpoons \text{Jd} + \text{Q}$ and $\text{Q} \rightleftharpoons \text{Cs}$ equilibria. (Starting material) $\Rightarrow$ [Result]: 1: $(\text{Ab} + \text{Jd} + \text{Q}) \Rightarrow [\text{Ab}]$; 2: $(\text{Ab} + \text{Jd} + \text{Q}) \Rightarrow [\text{Jd} + \text{Q}]$; 3: $(\text{Ab} + \text{Jd} + \text{Q}) \Rightarrow [\text{Jd} + \text{Cs}]$; 4: $(\text{Jd} + \text{Cs}) \Rightarrow [\text{Ab}]$; 5: $(\text{Jd} + \text{Cs}) \Rightarrow [\text{Jd} + \text{Cs}]$; 6: $(\text{Q}) \Rightarrow [\text{Q}]$; 7: $(\text{Q}) \Rightarrow [\text{Cs}]$; 8: $(\text{Cs}) \Rightarrow [\text{Q}]$; 9: $(\text{Cs}) \Rightarrow [\text{Cs}]$; 10: application of the two-capsules method (symbol centre marks the P - T parameters of the run).

Table 1. Comparison of the data on the reaction $\text{AB} \rightleftharpoons \text{Jd} + \text{Q}$.

$P(\text{kb})$ (at 600°C)	Equation boundary	Temperature Range (°C)	Apparatus	Reference
16.7	$P(\text{kb})0.71 + 0.0290 T^\circ\text{C}$	600 – 1105	Piston-cylinder	Mirwald and Massone (1980)
17.0	—	600	Calculation	Kelley <i>et al</i> (1953)
18.0	$6 + 0.0200$	800 – 1100	Hydrostatic	Birch and LeComte (1960)
16.7	—	600	Piston-cylinder	Newton and Smith (1967)
17.8	—	600	Piston-cylinder	Newton and Smith (1967)
16.5	—	600	Calculation	Hlabse and Kleppa (1968)
16.3	—	600	Piston-cylinder	Johannes <i>et al</i> (1971)
16.4	—	600	Hydrostatic	Hays and Bell (1973)
16.0	—	600	Piston-cylinder	Johannes (1978)
16.25	$0.35 + 0.0265$	600 – 1200	Piston-cylinder	Holland (1980)
16.4	$-1.33 + 0.0296$	1000 – 1096	Anvil-with-hole	Present study

*—extrapolated data

Table 2. Experimental results on the equilibria $\text{Ab Jd} + \text{Q}$ and Q Cs .

Run no	$T(^{\circ}\text{C})$	$P(\text{kb})$	Time (hours)	Starting material	Results
PC-19	1000	28.1	12.5	$\text{Ab} + \text{Jd} + \text{Q}$	$\text{Ab} + \text{Jd} + \text{Q}$
PC-35	1000	28.6	24.0	$\text{Ab} + \text{Jd} + \text{Q}$	$\text{Jd} + \text{Q Ab}$
PC*-46	1000	29.5	1.5	Q	Q
				Cs	Q
PC*-60	1000	30.0	1.5	Q	$\text{Q} + \text{Cs}$
				Cs	$\text{Cs} + \text{Q}$
PC*-49	1000	30.5	2.0	Q	Cs
				Cs	Cs
PC*-70	1080	30.5	4.0	Q	Q
				$\text{Ab} + \text{Jd} + \text{Q}$	$\text{Ab} > \text{Jd} + \text{Q}$
PC*-71	1080	30.8	4.0	Q	QCs
				$\text{Ab} + \text{Jd} + \text{Q}$	$\text{Jd} + \text{Q Ab}$
PC*-72	1080	31.1	4.0	Q	$\text{Cs} > \text{Q}$
				$\text{Ab} + \text{Jd} + \text{Q}$	$\text{Jd} + \text{Q Ab}$
PC*-52	1100	31.0	4.0	Q	Q
				$\text{Ab} + \text{Jd} + \text{Q}$	$\text{Ab} > \text{Jd} + \text{Q}$
PC-26	1100	31.5	10.0	$\text{Ab} + \text{Jd} + \text{Q}$	$\text{Jd} + (\text{Q}, \text{Cs}) > \text{Ab}$
PC*-96	1160	31.0	2.0	Q	Q
				$\text{Jd} + \text{Cs}$	$\text{Ab} > \text{Jd} + (\text{Q}, \text{Cs})$
PC*-95	1160	31.75	2.0	Q	$\text{Cs} + \text{Q}$
				$\text{Jd} + \text{Cs}$	$\text{Jd} + (\text{Cs} + \text{Q}), \text{Ab}$
PC*-53	1160	31.75	1.6	Q	Q
				$\text{Ab} + \text{Jd} + \text{Q}$	$\text{Ab} + \text{Jd} + \text{Q}$
PC*-51	1160	32.0	1.6	Q	Cs
				$\text{Ab} + \text{Jd} + \text{Q}$	$\text{Jd} + (\text{Cs}, \text{Q})$
PC*-43	1200	31.5	1.0	Q	Q
				Cs	Q
PC*-54	1200	32.0	1.2	Q	Q
				$\text{Ab} + \text{Jd} + \text{Q}$	$\text{Ab} > \text{Jd} + \text{Q}$
PC*-56	1200	32.5	1.8	Q	Cs Q
				$\text{Ab} + \text{Jd} + \text{Q}$	$\text{Jd} + (\text{Cs}, \text{Q}) > \text{Ab}$
PC*-58	1200	33.0	1.7	Q	Cs
				$\text{Ab} + \text{Jd} + \text{Q}$	$\text{Jd} + (\text{Cs}, \text{Q})$
PC*-39	1200	33.0	1.0	Q	Cs
				Cs	Cs
PC*-61	1400	34.0	0.5	Q	Q
				Cs	Q
PC*-62	1400	34.8	0.5	Q	Cs
				Cs	Cs

*—runs where the two-capsules method was used (refer text)

the present data. A possible explanation of this could be that the pressure distribution in the working part of the cell as investigated earlier is not uniform.

4. Discussion

The two-capsule technique allowed determination of the temperature of intersection of the two equilibrium curves $\text{Q} \rightleftharpoons \text{Cs}$ and $\text{Ab} \rightleftharpoons \text{Jd} + \text{Q}$ very accurately with a high

Figure 2. Results of various investigators on the quartz-coesite transition and albite breakdown reaction. References: 1: Johannes (1978); 2: Holland (1980); 3: Johannes *et al* (1971); 4: Hays and Bell (1973); 5: Hlabse and Kleppa (1968); 6: Newton and Smith (1967); 7: Mirwald and Massone (1980); 8: Kelley *et al* (1953); 9: Newton *et al* (1968); 10: Birch and LeComte (1960); 11: Mirwald and Massone (1980); 12: Birch and LeComte (1960); 13: Weaver *et al* (1979); 14: Bohlen and Boettcher (1982); 15: Present work; 16: Akella (1979); 17: Akella (1978).

degree of precision. In the temperature measurements there was no change in the reading of the thermocouples during the experiments.

The data on the temperature of intersection of the two aforesaid equilibrium curves enable us to comment on P - T pressure calibration by different workers. The intersection point as determined by various independent investigators will be similar only if the true equilibrium parameters have been determined, or else it can be assumed that the same systematic error has been made in the measurement of pressure and temperature.

Let us consider the results of previous investigations presented in figure 2 and tables 1 and 2.

In our experiments the two wires of thermocouples were of Pt-Rh alloys of different compositions, whereas in other studies Pt_{100} -(Pt-Rh) thermocouples were used.

Unfortunately, at present, there are no generally accepted corrections for the effect of pressure on the e.m.f. According to the available data (Getting and Kennedy 1970) this correction amounts to about 20°C (within the P - T range of our investigation) if the Pt/Pt-Rh thermocouple is used. While bracketing the reactions $\pm 20^\circ$ has been assumed for our measurements in order to take into account the effect of pressure on the e.m.f. of different thermocouples.

The results compared in table 3 indicate good agreement with the results reported by Mirwald and Massonne (1980). Applying our proposed method, the comparison of P - T calibration data seems (using $Ab \rightleftharpoons Jd + Q$ and $Q \rightleftharpoons Cs$ equilibria curve) impracticable at present, because data on the high albite breakdown reaction within

Table 3. Comparison of the data on the equilibria $\text{Ab} = \text{Jd} + \text{Q}$.

Investigators		Calculated P - T parameters of cross-point	
$\text{Ab} = \text{Jd} + \text{Q}$	$\text{Q} = \text{Cs}$	$P(\text{kb})$	$T(^{\circ}\text{C})$
1	3	31.9	1125
1	4	32.7	1153
1	1	31.6	1114
1	5	39.0	1057
1	6	33.7	1188
1	*	31.1	1098
2	3	32.8	1226
2	4	33.8	1264
2	1	32.6	1216
2	5	30.6	1142
2	6	35.6	1330
*	*	32.4	1208
*	3	31.9	1123
*	4	32.7	1149
*	1	31.6	1112
*	5	29.9	1057
*	6	33.7	1183
*	*	31.1	1096

Data from: 1—Hirwald and Massone (1980); 2—Holland (1980); 3—Akella (1978); 4—Akella (1979); 5—Bohlen and Boettcher (1982); 6—Weaver *et al* (1979); *—Present study.

the P - T range of our study are scarce. Except for our data as well as that of Mirwald and Massonne (1980) and Holland (1980) no other data are available for comparison. The data presented in the first two studies essentially differ from the third one. The discrepancy at 1100°C exceeds 1.5 kb due to corrections in pressure measurements and, therefore, deserves special attention.

Before discussing the discrepancy, it should be mentioned that comparison of the data on the high albite breakdown reaction is possible only if the equally-ordered albite was used in all experiments. Otherwise, there would be a considerable discrepancy between the equilibrium boundaries which do not depend only on the pressure measurements. Analyses of the available experimental and thermochemical data on the breakdown reaction (in connection with albite disordering) has been made by Hemingway *et al* (1981). The analysis confirms that (i) maximum albite disordering can be viewed only at temperatures near the melting point; (ii) there is no albite ordering under dry conditions with decreasing temperature and within the time required to conduct the experiments; (iii) the maximum disordered albite cannot be formed from the $\text{Jd} + \text{Q}$ mixture. The latter helps to explain the discrepancy between our data and that of Holland (1980), who reported that his runs at and above 1100°C cannot be considered reversed, as the albite breakdown to jadeite + quartz during the approach to the final P - T conditions. This implies crystallization of newly nucleated albite with unknown ordering during experiments rather than the totally disordered albite used in the starting material. Albite remained unaffected in our experiments,

because while approaching equilibrium P – T condition the starting albite remained stable. This may be the possible interpretation for the discrepancy observed in these data.

On the other hand one should consider that our experiments are not reversible. Contrary to the results of Holland (1980), Jd and Q in our starting mixture reacted to produce albite during the approach of the final P – T conditions. It follows from the data of Hays and Bell (1973) that at 600°C, albite synthesis and its breakdown reaction can take place under different pressures of 16.2 and 16.7 kb, respectively. It is quite probable that the reaction $\text{Ab} \rightleftharpoons \text{Jd} + \text{Q}$ is characterized by a certain hysteresis curve which can be considered to be responsible for the discrepancy between the data of Holland and our results. This problem can be resolved comparing piston-in and piston-out run data, but in the anvil-with-hole apparatus, outstroke procedures are practically impossible. In the piston-cylinder apparatus the friction corrections for the piston-in and piston-out runs are inadequate, these add to the uncertainties of pressure estimation.

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