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High-pressure behavior of kyanite: Decomposition of kyanite into stishovite and corundum

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ABSTRACT

The pressure stability of kyanite was experimentally reversed with the use of a multi-anvil apparatus. Kyanite was found to decompose into its oxides stishovite and corundum between 14 ± 0.5 GPa (at 1000 °C) and 17.5 ± 1.0 GPa (at 2000 °C).

Reliable thermodynamic calculations can be performed to temperatures of approximately 1500 °C. Up to this temperature, the location of the equilibrium kyanite = corundum + stishovite, determined in this study, constrains the equilibrium coesite = stishovite. A set of thermodynamic data was calculated by linear programming from the kyanite breakdown reaction and the coesite = stishovite equilibrium. Feasible values for the fitted thermodynamic properties are −28.5 to −26.3 MPa/K for the temperature derivative of the bulk modulus $[(dK/dT)_P]$ of kyanite, −815254 to −813635 J/mol for $G^0_{(1298)}$ of stishovite, and 24.6 to 26.3 J/mol · K for $S^0_{(1298)}$ of stishovite.

The experimental results indicate (1) that in peraluminous eclogites of basaltic or sedimentary origin, stishovite may coexist stably with corundum at a depth greater than 420–450 km and (2) that in an inhomogeneous Al-enriched mantle, corundum could be a minor constituent in the lower mantle.

INTRODUCTION

Kyanite, the high-pressure Al_2SiO_5 polymorph, is common in peraluminous eclogites of sedimentary and magmatic origin. The abundance of kyanite in eclogites remains approximately constant with increasing pressure until eclogite begins to transform to garnetite. At approximately 7 GPa, garnet becomes majoritic, and, consequently, its modal abundance increases while the amount of clinopyroxene decreases until clinopyroxene disappears around 15 GPa, leaving a stishovite-bearing garnetite (Irifune et al. 1986). Thus, although garnet becomes less aluminous with pressure, the drastic increase in modal abundance allows all Al_2O_3 present in a mid-ocean ridge basaltic eclogite to be incorporated in garnet (Irifune et al. 1986). However, for peraluminous compositions it remains yet unresolved if garnet could incorporate all Al or if a separate Al-rich phase coexists with garnet + stishovite.

In an average mantle composition, with increasing pressure Al is hosted by plagioclase, spinel, garnet, and an ilmenite-structure compound. When the garnet structure or ilmenite structure or both become unstable near the 670 km discontinuity, magnesiowüstite + perovskite forms. In a pyrolite mantle perovskite is capable of incorporating all Al_2O_3 present (Irifune 1994); however, in an Al-enriched inhomogeneous mantle a separate alumina phase, possibly kyanite or corundum, may coexist (see Ringwood 1991).

The aim of this experimental study is to clarify the high-pressure stability of kyanite and to determine whether kyanite decomposes with pressure into its oxides or forms a new Al_2SiO_5 polymorph. This work is the second part of a joint study on the high-pressure behavior of kyanite; the first part (Comodi et al. 1997) examines the structural evolution of kyanite with pressure.

Previous experimental investigations have come to the following results: Kennedy (1961) found that kyanite transforms to a new Al_2SiO_5 polymorph, called ‘‘kyanite II,’’ at 1–3 GPa. This result could never be reproduced and was questioned by Liu (1974) who performed a diamond-anvil experiment on a kyanite starting material. At a temperature between 1000 and 1400 °C, kyanite was found to decompose to stishovite + corundum around 16 GPa. Liu (1974) estimated the slope of reaction from the thermodynamic tables of Robie and Waldbaum (1968) and concluded that the equilibrium

$$1 \text{ kyanite} = 1 \text{ stishovite} + 1 \text{ corundum} \qquad (1)$$

is located at P (GPa) = (13.5–17.1) + 0.0011 T (K). At much larger pressures, i.e., at 40–70 GPa, Ahmed-Zaïd and Madon (1991) reacted various starting materials at

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approximately 2200 °C and obtained a high-pressure polymorph of Al_2SiO_5 with the V_2O_5 structure.

A recent experimental determination of Equilibrium 1 by Irifune et al. (1995) is discussed below.

EXPERIMENTAL TECHNIQUES

Apparatus

Experiments were conducted in a split-sphere multi-anvil device. To pressures of 15.5 GPa, octahedra with an edge length of 14 mm (14M) were employed on an 8 mm truncation (TEL); cubes had edges 32 mm long. From 16.0 GPa to 19.0 GPa octahedra with a 10 mm (10M) edge length were used on a 5 mm truncation. For the 14M octahedra, pressure was initially calibrated against coesite-stishovite as determined by Yagi and Akimoto (1976) and against the α-β phase transition in Mg_2SiO_4 (Katsura and Ito 1989). However, pressures were recalculated according to the determination of the coesite-stishovite equilibrium by Zhang et al. (1996). Fortunately, the coesite-stishovite equilibria of Yagi and Akimoto (1976) and Zhang et al. (1996) intersect at approximately 1250 °C, which is relatively close to the calibration temperature of 1200 °C. Thus, recalculation of the experimental pressures in this study employing Zhang et al. (1996) instead of Yagi and Akimoto (1976) yields a correction of −0.1 GPa at 9.0 GPa and a negligible difference at 14.5 GPa. For the 10M octahedra, pressure was calibrated (Canil 1994) against α -β and β -γ transitions in Mg_2SiO_4 (Akaogi et al. 1989). The absolute pressure uncertainty of the multi-anvil apparatus is commonly estimated to ± 4%; however, the reproducibility is approximately 0.1 GPa. Stepped $LaCrO_3$ furnaces were employed in the 14M octahedra; a straight $LaCrO_3$ heater was used in the 10M octahedra. A Pt-$Pt_{90}Rh_{10}$ S-type thermocouple was employed for experiments to 1300 °C, whereas at higher temperatures a $W_{97}Re_3$-$W_{75}Re_{25}$ thermocouple was used. A pressure correction on the thermocouple emf was not undertaken. Temperature gradients were of the order of 40–60 °C (at 1000–1600 °C) with the stepped heater, whereas at 2000 °C temperature gradients in the straight heater were approximately 100 °C over the capsule length. Temperatures listed in Table 1 are thermocouple readings and represent the almost coldest spot within a capsule. Capsules had initial lengths of 1.5 mm in the 14M and 1.0 mm in the 10M octahedra. For experiments below 1900 °C, platinum capsules were not welded but folded at the upper end. For experiments at higher temperatures capsules were folded from rhenium foil. After putting the octahedra together, the entire assemblages were held at 300 °C for several hours to ensure dry conditions.

The starting material was composed by 35 mol% synthetic stishovite, 29 mol% analytic-grade Al_2O_3 that was fired at 1800 °C, and 36 mol% natural kyanite. In the natural kyanite, trace elements such as Fe and Cr were below detection limit of an electron microprobe. Stishovite was synthesized from silica acid at 10.5 GPa, 950 °C.

TABLE 1. Experimental conditions and results

	P (GPa)	*T* (°C)	*t* (min)	Experimental products
1k-12	12.0	800	700	ky, stish, cor; no reaction
1k-17	13.0	1000	960	ky, stish(−)
1k-19	13.5	1000	910	ky, stish(−)
1k-18	14.0	1000	900	ky, stish, cor; no reaction
1k-20	14.5	1000	430	stish, cor, ky(−); stish+cor-growth
1k-21	15.0	1000	200	stish, cor
1k-5	14.0	1300	150	ky, stish(−)
1k-8	14.5	1300	180	ky, stish, cor; ky-growth
1k-3	15.0	1300	150	stish, cor
1k-2	16.0	1300	95	stish, cor
1k-16	15.5	1550	35	ky, stish, cor; capsule zoned
1k-9	15.5	1900	20	ky, stish(−)
1k-11	16.0	1900	12	ky, stish(−)
1k-13	17.0	2000	15	ky, stish(−)
1k-22	18.0	2000	12	stish, cor
1k-14	19.0	2000	10	stish, cor
1k-4	14.0	2100	11	ky, stish(−)
1k-7	15.5	2100	13	ky, stish(−)
1k-15	18.0	>2300	10	cor, $Al_2Si_2O_7$

Note: cor = corundum, ky = kyanite, stish = stishovite. (−) indicates that minor amounts were present.

Experimental charges were analyzed by X-ray diffraction or electron microprobe analysis, although experiment products were easily identifiable by their color and hardness when extracting them from the capsules. Experiments resulting in kyanite yielded relatively soft, often slightly bluish powders, whereas stishovite + corundum constituted extremely hard white cylinders that survived stripping the noble metal capsules without breaking. Longitudinal sections of experimental charges that were suspected to be on the reaction boundary were analyzed with an electron microprobe in order to detect possible zonations in the capsules.

Experimental results

Reaction in most experimental charges was complete (Table 1), at least at the detection limit of X-ray diffraction (ca. 3%). Experimental charges examined by microprobe proved to be homogeneous with one exception: experiment lk−16 (1550 °C, 15.5 GPa) yielded stishovite + corundum at the cold ends of the capsule and kyanite at the relative warm center of the capsule. Thus, at 15.5 GPa, the breakdown reaction of kyanite occurs between 1550 °C and ca. 1610 °C.

Two experiments (lk-20 and lk-8), which were directly prepared for X-ray diffraction, yielded kyanite and stishovite + corundum as experimental products. Unfortunately, we could not determine whether if the presence of kyanite and stishovite + corundum resulted from incomplete reaction or from zonation within the capsule. However, an overall direction of reaction resulted unambiguously from comparison of relative X-ray diffraction peak heights of starting material and experimental products (Table 1).

In two experiments, reaction could not be detected, neither by electron microprobe analysis nor by comparing relative X-ray diffraction peak heights of starting material

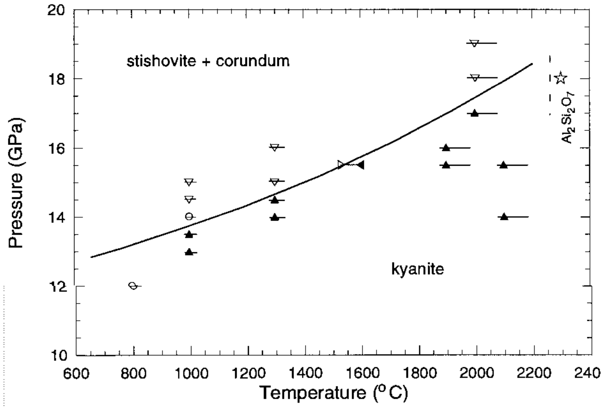

FIGURE 1. Experimental results on the equilibrium kyanite = stishovite + corundum. Full triangles: kyanite; open triangles: stishovite + corundum; circles: no reaction; star: $Al_2Si_2O_7$ + corundum. Bars represent approximate thermal gradients over the capsule length.

and experimental run products. At 800 °C (lk-12, Table 1) temperature was obviously too low to permit reaction in a dry $Al_2O_3-SiO_2$ system, and at 1000 °C, 14 GPa (lk-18) it is most likely that this condition is too close to the equilibrium boundary to permit significant reaction at this still relative low temperature.

Because the starting material was composed exclusively by the phases participating in the investigated reaction, our results represent true experimental reversals and should not have been effected by nucleation problems.

Principally, the present study confirms the diamond anvil experiment from Liu (1974); kyanite was found to decompose into its oxides stishovite and corundum instead of forming a new high pressure Al_2SiO_5 polymorph. Reaction 1 was experimentally investigated at 1000, 1300, 1550, and 2000 °C (Fig. 1, Table 1). Up to 2100 °C, other phases then kyanite, stishovite, and corundum have not been observed, neither by X-ray diffraction nor by electron microprobe. A single experiment (lk-15) was performed at a temperature of more than 2300 °C (18 GPa). At this temperature the thermocouple broke, but heating was continued to a heating power equivalent to about 2500 °C (± 100 °C). This experiment yielded $Al_2Si_2O_7$ + corundum as a breakdown product of kyanite. A phase with $Al_2Si_2O_7$ stoichiometry was also observed by Ahmed-Zaïd and Madon (1990).

The phase boundary between kyanite and its oxides can be approximated by P (GPa) $\approx 9.3 + 0.0035\ T$ (K). The absolute pressure uncertainty on this reaction is about ± 0.5 GPa at 1000 °C and is not larger than ± 1.0 GPa at 2000 °C.

DISCUSSION OF EXPERIMENTAL RESULTS

Our experimental results disagree with the multi anvil study of Irifune et al. (1995) undertaken in the temperature range of 1000–1500 °C. Equilibrium 1 was located by Irifune et al. (1995) 1.5 GPa (1000 °C) to 2.0 GPa (1500 °C) lower than in our study. The experimental setup of both studies is quite similar: pressure calibrations were identically against coesite-stishovite and α-β Mg_2SiO_5 at 1200 °C. Thus the relative pressure uncertainties between the two experimental studies should be less than 0.2–0.3 GPa. However, for the pressure range of 10–15.5 GPa the anvil truncation (TEL) used in this study (8 mm TEL) is significantly larger than that used by Irifune et al. (3.5 mm TEL). Our larger octahedra and truncation edge length results in a higher precision of pressure. The thermocouple reading of Irifune et al. (1995) had to be corrected because WC cubes were used as part of the thermocouple. This introduces a small additional uncertainty in temperature. However, because Equilibrium 1 is mostly pressure dependent, this can explain only a small fraction of the difference between the two studies. The observed reaction kinetics of the dry $Al_2O_3-SiO_2$ system is identical in both studies: reaction below 1000 °C was not obtained, and at ca. 1500 °C, complete reaction occurs fast.

A principal difference between the two experimental studies arises from the Fe content of the natural kyanite used as a starting material. Whereas our kyanite is almost Fe free (<0.02 wt% Fe_2O_3), the kyanite of Irifune et al. (1995) contained 0.5 wt% Fe_2O_3, equivalent to 0.5 mol% Fe_2SiO_5 component in kyanite. If both, kyanite and corundum have similar activity-composition (a-x) relationships, then the Fe impurity does not affect the position of Equilibrium 1. If the Fe impurity should account for the 1.5–2.0 GPa difference in experimentally determined pressures of Reaction 1, then the activity of corundum would have to be lowered to $a_{cor} \approx 0.75$ while the activity of kyanite remains close to $(1-x_{Fe_2SiO_{5\div\}}})$. However, as long as the a-x relationships of kyanite and corundum remain unknown, we cannot quantify the effect of Fe on Equilibrium 1.

The bulk modulus of 202 ± 15 GPa (with $K' = 4$) for kyanite calculated by Irifune et al. (1995) is significantly higher than the measured bulk modulus of 160 GPa (with $K' = 4$, Comodi et al., this volume). This might be interpreted as the result of the lower pressure of Equilibrium 1 determined by Irifune et al. (1995). A calculation with all thermodynamic properties remaining constant except a change in the bulk modulus of kyanite from 160 to 202 GPa yields a pressure decrease of 0.9–1.0 GPa for Equilibrium 1. Thus, the overestimation of the bulk modulus of kyanite is consistent with the lower pressures of Equilibrium 1 as determined by Irifune et al. (1995). Employing the measured $K_{T(\mathrm{kyanite})}$ ($K_{T(298)} = 156$ GPa, $K' = 5.6$; Comodi et al. 1997) and measured ΔH^0 of stishovite = coesite (Akaogi et al. 1995, Liu et al. 1996), Equilibrium 1 cannot be calculated to the experimental determined position of Irifune et al. (1996).

Several differences exist between the two experimental studies none of them alone explains the large difference in equilibrium pressure for the kyanite decomposition reaction. For the moment, we conclude that this discrepancy remains unresolved; however, accumulated uncertainties in the study of Irifune et al. (1995) could explain

TABLE 2. Input parameters for calculations

	V^0_{1298} J/MPa	$K_{T(298)}$ GPa	K'	$(dK/dT)p$ MPa/K	α_0 ($\times$ 10^5)	α_1 ($\times$ 10^8)	α_2 ($\times$ 10^2)	α_3 ($\times$ 10^1)	G^0_{1298} J/mol	S^0_{1298} J/Mol·K	a	b	c ($\times$ 10^{-6})	d ($\times$ 10^{-8})
Kyanite	44.25*	156.0*	5.6*		2.443†		3.936		−2 444 441‡	82.30‡	272.61§	−2514.0	4.0438	−13.6049
Stishovite	14.01‖	315.0#	5.3#	−47**	1.053††	0.903		1.220			85.78††	−345.5	−3.6050	4.5110
Coesite	20.65‖	96.0‡‡	8.4‡‡	−20**	0.543‖	0.500			−852 530§§	40.15§§	78.90§§	−163.5	−5.0650	8.2500
α-quartz	22.69‖	37.4‖‖	6.4‖‖	−10‖‖	2.752‖	2.987		0.926	−856 288‖	41.46‖	80.01##	−240.28	−3.5467	4.9157
Corundum	25.58‖	253.0***	5.0***	−31†††	2.276‡‡‡	0.4198		−0.0897	−1 582 199##	50.82##	164.65§§§	−1254.6	0.1491	−3.9160

Note: $Cp = a + bT^{-0.5} + cT^{-2} + dT^{-3}$.

* Comodi et al. (1997).
† This study, fitted to data of Winter and Ghose (1979).
‡ Holland and Powell (1990).
§ This study, see text.
‖ Robie et al. (1978).
Baosheng et al. (1996).
** Watanabe (1980).
†† Akoagi et al. (1995).
‡‡ Levien and Prewitt (1981).
§§ This study, fit to experiments of Bohlen and Boettcher.
‖‖ Anderson et al. (1968).
Berman (1989).
*** Richet et al. (1988).
††† Average value from Goto et al. (1989).
‡‡‡ Fei (1995).
§§§ Richet and Fiquet (1991), refit from their preferred C_p-function to the C_p-function used in this study.

part of the pressure difference between the two experimental studies.

Calculation of phase boundaries

Most thermodynamic properties necessary to calculate Equilibrium 1 are well determined. However, some of them, such as the bulk modulus of kyanite and standard state enthalpy and entropy of stishovite were poorly constrained. In a parallel study (Comodi et al. 1997) the isothermal bulk modulus of kyanite was determined at room temperature by single crystal X-ray diffraction in a Merrill-Bassett type diamond anvil cell. Thus, standard state enthalpy and entropy of stishovite remain among the less accurate parameters and the above equilibria will be used to further constrain them.

Phase boundaries are calculated with the use of a Murnaghan equation of state for volumes at pressure and temperature.

$$V_{(P,T)} = V_{(1,T)}\left(1 + \frac{K'P}{K_T}\right)^{-1/K'} \tag{2}$$

Temperature dependance of molar volume at standard state pressure is expressed through

$$V_{(1,T)} = V^{\circ}_{298} \exp\left(\int_{298}^{T} (\alpha_0 + \alpha_1 T + \alpha_2 T^{-1} + \alpha_3 T^{-2})\, dT\right). \tag{3}$$

Temperature dependance of isothermal bulk modulus is calculated as

$$K_T = K_{T(298)} + (dK/dT)_P\,(T - 298) \tag{4}$$

where $K_{T(298)}$ is the isothermal bulk modulus at room temperature.

C_P functions for coesite and stishovite were measured from 300–700 K and calculated using the model of Kieffer (1979a, 1979b) by Akaogi et al. (1995). The C_P function for kyanite was measured by Pankratz and Kelley (1964) to 1800 K. To extend the temperature range, we fitted the C_P-function of kyanite to the measurements and asymptotically to the high temperature convergence of C_P given by

$$C_P = 3Rn + \alpha_T^2 K_T V_T T. \tag{5}$$

For the fit procedures we used linear programming to define the feasible region (Gordon 1973) describing all possible solutions for S^0_{stish} and G^0_{stish}. Consecutive fits were undertaken varying $(dK/dT)_P$ of kyanite in steps of 0.1 MPa/K. Other thermodynamic properties that were held constant during the fit are listed in Table 2. The experiments of this study on Equilibrium 1 and of Zhang et al. (1993 and 1996) on the transition of coesite to stishovite were fitted in the temperature range to 2000 °C. Derivation of thermodynamic properties through calculations at higher temperatures were avoided because of the increasingly large uncertainties of $(dK/dT)_P$ and $\alpha(T)$. Beside the experiments on Equilibrium 1 and coesite = stishovite, the calorimetric measurements of either Akaogi et al. (1995) or Liu et al. (1996) on ΔH^0 of coesite = stishovite were employed as upper and lower boundary for the Gibbs free energy of stishovite at standard state.

DISCUSSION OF RESULTING THERMODYNAMIC PROPERTIES

Feasible solutions for G^0_{stish}- S^0_{stish}-$(dK/dT)_P$ triplets are obtained for a range of G^0_{stish}, which overlaps with the calorimetric measurements of Akaogi et al. (1995). However, a feasible solution employing the calorimetric data of Liu et al. (1996) and the input data of Table 2 does not exist. In other words, the calorimetric measurements of Akaogi et al. (1995) are consistent with the experiments of this study and of Zhang et al. (1993, 1996). In contrast, the calorimetric measurements of Liu et al. (1996) are consistent

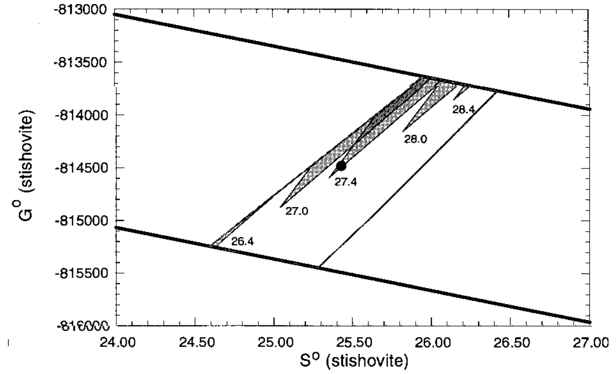

Figure 2. Feasible region of $S^0_{(1298)}$ and $G^0_{(1298)}$ of stishovite for different values of $(\mathrm{d}K/\mathrm{d}T)_P$ of kyanite (numbers at the lower left corner of shaded areas, in megapascals per kelvin). The thick lines represent limits on G^0_{stish} from calorimetry measurements of Akaogi et al. (1995). The area enclosed by the thick and thin lines represent feasible solutions if only calorimetric results and experiments on coesite = stishovite from Zhang et al. (1993, 1996) are considered. The shaded polygons represent feasible solutions for G^0_{stish}-S^0_{stish} pairs calculated from calorimetric results, experiments on coesite = stishovite and experiments on kyanite = stishovite + corundum for feasible values of $(\mathrm{d}K/\mathrm{d}T)_P$ of kyanite.

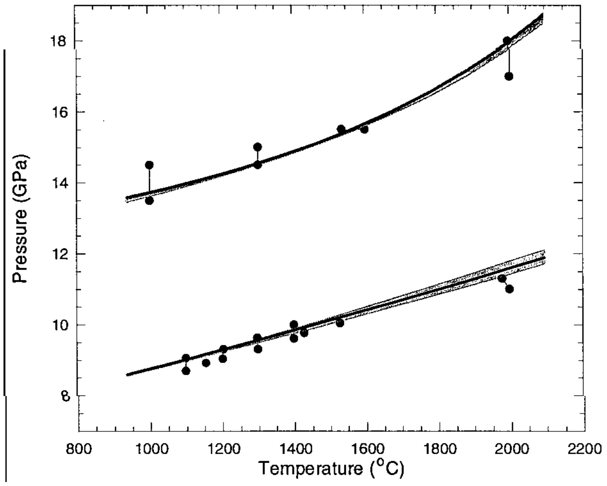

Figure 3. Experimental brackets on kyanite = stishovite + corundum from this study and on coesite = stishovite from Zhang et al. (1993, 1996). Thick lines represent the calculated reaction boundaries from our best fit (see Table 3). Shaded areas represent all possible *P-T*-loc of reaction boundaries as calculated from feasible thermodynamic properties (see text and Fig. 2).

with the experiments of Zhang et al. (1993, 1996) but not with the additional constraints on the properties of stishovite that result from our experimental determination of kyanite = stishovite + corundum.

As can be seen from Figure 2, feasible solutions satisfying the experiments and calorimetric measurements can be obtained with $(\mathrm{d}K/\mathrm{d}T)_{P(\mathrm{kyanite})}$ ranging from −26.3 to −28.5 MPa/K. The range of feasible values for G^0_{stish} and S^0_{stish} is given in Table 3. It should be pointed out that only certain combinations of $(\mathrm{d}K/\mathrm{d}T)_{P(\mathrm{kyanite})}$, G^0_{stish}, and S^0_{stish} within the ranges given in Table 3 are valid (see Fig. 2). We locate our preferred solution at the mean value of $(\mathrm{d}K/\mathrm{d}T)_{P(\mathrm{kyanite})} = -27.4$ MPa/K and at the mean value of the calorimetric measurements of H_{stish} from Akaogi et al. (1995). The position of the calculated equilibria and the experimental brackets on the equilibria are shown in Figure 3. The $\Delta V_{P,T}$ of reaction is −7.8% at 1000 °C and −5.8% at 2000 °C. Although experimental brackets at temperatures above 2000 °C on coesite = stishovite from Zhang et al. (1993) were not employed for the derivation of thermodynamic properties, it should be noted that we obtained only 90 °C difference between the calculated (2560 °C) and the experimentally determined position (ca. 2650 °C; Zhang et al. 1996) of coesite = stishovite at 13.5 GPa. This difference is largely within accumulated uncertainties of (1) experimental temperature and pressure and (2) uncertainties in the calculation mainly arising from the extrapolation of $\alpha(T)$ and the estimation of $(\mathrm{d}K/\mathrm{d}T)_{P(\mathrm{coesite})}$ by Watanabe (1980).

In our first calculations, we also used G^0_{coesite} and S_{coesite} as fit parameters and the equilibrium quartz = coesite as experimentally determined by Bohlen and Boettcher (1982). However, the experimental brackets are much narrower in this piston cylinder study than in any multianvil study, and as a consequence, G^0_{coesite} and S_{coesite} remain almost constant. We thus prefer a fixed G^0_{coesite} and S_{coesite} (Table 2).

In the following we discuss the most important uncertainty in the calculation $(\mathrm{d}K/\mathrm{d}T)_P$ and draw some consequences on the equilibrium coesite = stishovite.

Temperature derivative of bulk modulus

Because of experimental difficulties, direct measurements of the temperature derivative of the isothermal bulk

Table 3. Resulting standard state Gibbs free energy, enthalpy, and entropy of stishovite and temperature derivative of bulk modulus of kyanite

			Feasible region	
		Preferred solution	max.	min.
$G^0_{(1,298)\mathrm{stish}}$	(J mol^{-1})	−814 482	−813 633	−815 254
$H^0_{(1,298)\mathrm{stish}}$	(J mol^{-1})	−873 678	−872 668	−874 687
$S^0_{(1,298)\mathrm{stish}}$	(J mol^{-1} K^{-1})	25.42	26.25	24.62
$(\mathrm{d}K/\mathrm{d}T)_{P(\mathrm{kyanite})}$	(MPa K^{-1})	−27.4	−26.3	−28.5

Note: Not any combination of values within the feasible ranges is feasible; see Figure 2.

modulus $(\mathrm{d}K/\mathrm{d}T)_P$ are scarce. Values in the literature are either calculated from elastic property measurements at ambient pressures (Goto et al. 1989; Anderson and Isaak 1995), estimated from enthalpies following a method of Anderson (1989), or calculated through fitting phase equilibria (e.g., Fei et al. 1990). A direct measurement of $(\mathrm{d}K/\mathrm{d}T)_P$, which allows comparison of indirectly calculated values with direct experimental measurements was performed for $MgSiO_3$ perovskite by Funamori et al. (1996). For this example, the measurements at P and T yielded -28 ± 3 MPa/K (1 σ). However, Funamori et al. (1996) argue that an error including all uncertainties amounts to $\pm$ 17 MPa/K. Despite this large error, the measured $(\mathrm{d}K/\mathrm{d}T)_{P(\mathrm{perovskite})}$ is significantly smaller than the value of -55 MPa/K obtained from fitted phase equilibria (Fei et al. 1990) or of -70 MPa/K as calculated by Saxena and Shen (1992) following a method of Anderson (1989). This large discrepancy between experimentally measured and calculated values for $(\mathrm{d}K/\mathrm{d}T)_{P(\mathrm{perovskite})}$ suggests that large uncertainties exist for any calculated $(\mathrm{d}K/\mathrm{d}T)_P$.

Unfortunately, $(\mathrm{d}K/\mathrm{d}T)_P$ has a large influence on the calculated position of a given phase boundary. This significant influence may be quantified through a calculation where all parameters are held constant except of $(\mathrm{d}K/\mathrm{d}T)_{P(\mathrm{kyanite})}$. A difference of $-5/+5$ MPa/K for $(\mathrm{d}K/\mathrm{d}T)_{P(\mathrm{kyanite})}$ results in a shift of Equilibrium 1 of $-0.2/+0.3$ GPa at 1000 °C and of $-1.4/+2.3$ GPa at 2000 °C. Thus, reliable calculations are possible at relatively low temperatures but only semiquantitative results can be presented for mantle temperatures.

We also fitted the experiments employing identical values for $(\mathrm{d}K/\mathrm{d}T)_P$ for all participating phases, but a feasible solution was not obtained. Thus we employ values for $(\mathrm{d}K/\mathrm{d}T)_P$ of stishovite and coesite from Watanabe (1980) and for corundum from Goto et al. (1989) (see Table 2). With these $(\mathrm{d}K/\mathrm{d}T)_P$ values, we obtain feasible solutions for $(\mathrm{d}K/\mathrm{d}T)_P$ kyanite ranging from -26.3 to -28.5 MPa/K. At present state, a better solution than such a fit is not available, however, we like to emphasize that this result is mostly the consequence of the values for $(\mathrm{d}K/\mathrm{d}T)_P$ chosen for the other phases in the equilibria. It remains undetermined, whether the obtained range for $(\mathrm{d}K/\mathrm{d}T)_{P(\mathrm{kyanite})}$ has crystallographic relevance.

THERMODYNAMIC PROPERTIES OF STISHOVITE

Recently Zhang et al. (1996) performed experimental reversals on the equilibrium coesite = stishovite employing a cubic multi anvil. Pressures were determined by insitu diffraction of NaCl and are cited to be more accurate than 0.2 GPa. The study of Zhang et al. (1996) yields a $\mathrm{d}P/\mathrm{d}T$ slope for coesite = stishovite of 2.6 MPa/K, which is significantly larger than 1.1 MPa/K as previously determined by Yagi and Akimoto (1976). Only few of the experiments of Yagi and Akimoto (1976) represent true reversals; Zhang et al. (1996) argue that these true reversals are in agreement with their results, but that some of the other experiments of Yagi and Akimoto (1976) are not in equilibrium because of the low temperatures (600–800 °C) and because of the use of amorphous SiO_2 as starting material.

Shergiou et al. (1995) determined the coesite-stishovite transition in a laser-heated diamond-anvil cell (DAC) at temperatures of 2300–2630 °C. They found that coesite transforms to stishovite at 10.6 GPa (at 2500 °C), which is 2.4 GPa lower as determined by Zhang et al. (1993). The $\mathrm{d}P/\mathrm{d}T$ slope of 1.0 MPa/K as proposed by Shergiou et al. (1995) is consistent with that of Yagi and Akimoto (1976). However, Fiquet et al. (1996) showed that accurate pressure determinations in laser-heated diamond anvil cells are difficult, because heating of the central part of a DAC causes a local increase of pressure. This increase is not transmitted to the cold outer part of the DAC where the ruby employed for pressure determination is situated. Fiquet et al. (personal communication) also showed that experiments performed at pressures nominally 3 GPa below the coesite-stishovite transition (pressures determined by ruby fluorescence in the cold outer part) yielded stishovite in the heated central part. Thus, diamond-anvil studies at high temperatures significantly underestimate the pressure to which the samples are exposed. Such a pressure underestimation would explain the difference between the DAC study of Shergiou et al. (1995) and the multi-anvil studies of Zhang et al. (1993).

Our results on the equilibrium kyanite = stishovite + corundum are consistent with the $\mathrm{d}P/\mathrm{d}T$ slope and the experimental location of coesite = stishovite as determined by Zhang et al. (1993, 1996). Calculation of these phase equilibria results in a consistent set of thermodynamic properties for all phases. In contrast, such a consistent set of thermodynamic properties cannot be found if the location of coesite = stishovite as proposed by Yagi and Akimoto (1976) and Shergiou et al. (1995) is employed. This result is obtained from calculations at temperatures of 1000 to 1300 °C, as shown above, the uncertainties in $(\mathrm{d}K/\mathrm{d}T)_P$ do still permit precise constraints at these relatively low temperatures.

CONCLUDING REMARKS

The present experiments on the kyanite breakdown reaction define at which depth corundum stably coexists with a SiO_2 polymorph. In an appropriate bulk composition, corundum could coexist with stishovite at pressures of the transition zone and the lower mantle. In subducted eclogites with an Al excess with respect to majoritic garnet, kyanite decomposes to corundum stishovite at depth of 400–450 km. Modal abundances of kyanite are low in most basaltic eclogites (0–10 vol%), and thus, the reduction of volume resulting from decomposition of kyanite remains negligible; it amounts to less than 0.5% densification in eclogites.

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