

THE EFFECT OF PRESSURE AND TEMPERATURE ON PHASE STABILITY OF TRICALCIUM SILICATE

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Using the condition for an equilibrium of the solid state reaction and by means of Clausius—Clapeyron equation, an evaluation was made of the stability limit of Ca_3SiO_5 in the P — T diagram in the pressure region of up to 0.8 GPa. The differential quotient dT/dP for the reaction $\text{Ca}_3\text{SiO}_5 \rightarrow \text{Ca}_2\text{SiO}_4 + \text{CaO}$ has a slope of 550 K/GPa. The metastability region of Ca_3SiO_5 was verified experimentally.

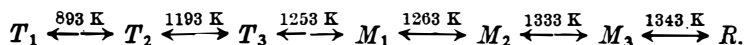
INTRODUCTION

Tricalcium silicate, Ca_3SiO_5 ($3 \text{ CaO} \cdot \text{SiO}_2 = \text{C}_3\text{S}$) is the essential component of portland cement. At normal temperature and under normal pressure it is a metastable phase. In the literature, the bottom limit of the temperature stability region under normal pressure is given over a wide temperature interval from 1248. to 1670 K [1—4] with the most probable limit value of 1525 K [1]. Below this limit temperature, tricalcium silicate decomposes according to the equation



The decomposition proceeds at a satisfactory rate at higher temperatures only. The slow decomposition rate at lower temperatures renders possible the occurrence of a metastable form of C_3S . The compound melts incongruently. An incongruent decomposition to $\text{CaO} +$ liquid phase takes place at about 2423 K [1].

Within the metastability temperature range, C_3S occurs in seven polymorphous modifications, which have been identified by X-ray analysis, microscopically and by means of DTA in three triclinic (T), three monoclinic (M) and in one rhombohedral (R) modifications [5, 6]:



All the polymorphous transformations are reversible with a low enthalpy of the transformation. The $T_1 \leftrightarrow T_2$ inversion exhibits hysteresis [5, 6]. Some of the high-temperature forms can be stabilized by formation of solid solutions. The most extensive studies on the formation of C_3S solid solutions and on limit concentrations of some oxide admixtures can be found in [6—14].

Crystal structure analysis of the triclinic form of C_3S (T_1) has proved that tricalcium silicate is a defined compound [15] and not a solid solution of CaO in Ca_2SiO_4 [16]. The most significant structural data are as follows [15]: space group $\text{P}\bar{1}$, $a = 11.67$, $b = 14.24$, $c = 13.72 \times 10^{-10}$ m, $\alpha = 105^\circ 30'$, $\beta = 94^\circ 20'$, $\gamma = 90^\circ$, $Z = 18$, $V = 2190.3 \times 10^{-30}$ m³, $D_x = 3.115$ Mg/m³. The structural formula can be written in the form: $^{\text{VII}}\text{Ca}_6^{\text{VI}}\text{Ca}_{48}^{\text{IV}}\text{Si}_{18}^{\text{VI}}\text{O}_{18}^{\text{VO}_6}\text{VO}_{66}$, where the Roman numerals left to the element designation indicate the coordination number of the respective atom. The CaO_6 and CaO_7 polyhedrons are irregular and joined

into a massive three-dimensional skeleton first of all by means of common edges. The SiO_4 tetrahedrons are situated in the gaps of this skeleton. Each tetrahedron apex serves as common apex to further three or four CaO_6 or CaO_7 polyhedra. Of the total number of 90 oxygen atoms, 72 atoms comprise a component of the SiO_4 tetrahedra. Each of the 18 oxygen atoms belonging solely to calcium polyhedra, forms an apex for six CaO_n polyhedra.

The present study had the aim to study the effect of pressure and temperature on phase stability of tricalcium silicate.

EXPERIMENTAL

The tricalcium silicate specimen employed in the high-pressure experiments had the quality of a standard (FRG). The high-temperature experiments were carried out with a specimen of C_3S syntetized from CaCO_3 of A. R. purity and with Brazilian quartz at 1875 K [17]. The $\gamma\text{-Ca}_2\text{SiO}_4$ used in the high-pressure experiments was of A. R. purity. Neither microscopic nor X-ray phase analysis succeeded in identifying the presence of other polymorphous modifications [41].

The X-ray phase analysis of the specimens from high-pressure and high-temperature experiments was carried out on the Philips PW 1050 apparatus using $\text{CuK}\alpha$ radiation. The diffraction angles of the indexed X-ray patterns were used for refinement the lattice parameters by means of the least squares method on the CDC 3300 computer by means of the POWDER program [18]. The high-pressure experiments were carried out in a "belt" type high-pressure apparatus with an internal resistance graphite heating. Following compression, the C_3S specimens were heated within several minutes in one or several temperature cycles (thus preventing the chamber from overheating) up to the required temperature. Following each cycle, the specimen was rapidly cooled by switching off the resistance heating, so that the specimen temperature fell from 1100 K down to 300 K within 10 seconds (Table II). The temperature measurement was indirect. The current density, calibrated at the known melting points of substances, allowed to determine the temperature with an accuracy of $\pm 10\text{--}20$ K according to the height of the temperature being measured. In all the high-pressure and temperature experiments, the C_3S specimens in the reaction space of the "belt" were sealed in a platinum tube provided with boron nitride stoppers (Table II).

The high-pressure experiments with $\gamma\text{-Ca}_2\text{SiO}_4$ were arranged similarly, but with a slower heating and direct specimen temperature measurement under

Table I
The effect of heating on stability of Ca_3SiO_5 under normal pressure

Experi- ment No.	Heating temperature T K	Time of heating τ h	Decomposition products
1.	1270	0.5	traces of CaO
2.	1470	77.0	$\beta\text{-Ca}_2\text{SiO}_4 + \text{CaO}$
3.	1570	100.0	without decomposition

pressure using a chromel-alumel thermocouple (Table III). In this instance, the temperature measurement accuracy was ± 7 K. The deviations were affected by temperature gradients and by the pressure dependence of the thermocouple EMF. The pressure calibration of the "belt" was carried out in a standard way by measuring electrical conductivity of standards with an accuracy of ± 3 %. Compression of the specimens at room temperature was performed between Bridgman's anvils from tungsten carbide and in the high-pressure XKB-100 X-ray camera produced by MRC (USA), using $\text{MoK}\alpha$ radiation. In order to assess the influence of pressure on C_3S decomposition kinetics, the specimens were heated rapidly to the chosen temperature under normal pressure, and then rapidly quenched by dropping into a copper block (Table I).

RESULTS AND DISCUSSION

The effect of high pressure on the direction of the solid phase reaction (1)

The effect of high pressure on the direction of the reaction (1) can be elucidated by means of the P - T diagram of C_3S (Fig. 1). At temperatures exceeding the lower stability limit of C_3S (1525 K), the reaction (1) proceeds in the direction of tricalcium silicate synthesis from the components CaO and Ca_2SiO_4 (Table I, experiment No. 3). When these temperatures are combined with a satisfactory high pressure, reaction (1) changes its direction and proceeds towards decomposi-

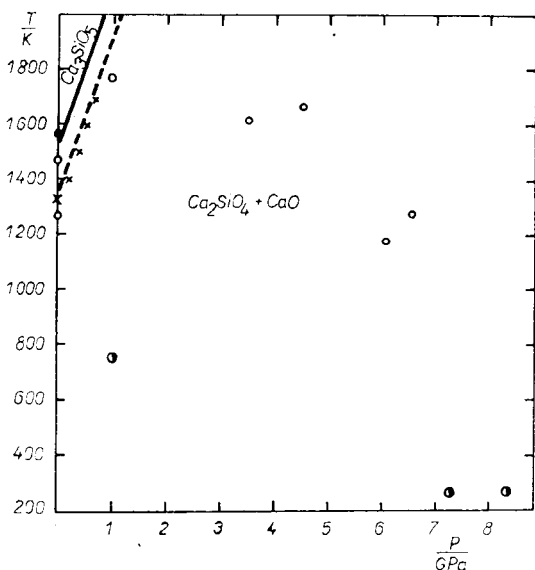


Fig. 1. Stability limit of Ca_3SiO_5 in the P - T diagram. Points + delimitate the stability field of Ca_3SiO_5 by means of the equilibrium condition (3). The slope of the dashed straight line passing through points (+) is the differential quotient dT/dP , determined by means of equation (4). The full line parallel with the slope dT/dP passes from point $T_{\text{eq}} = 1525$ K, $P_{\text{eq}} =$ normal pressure established experimentally. The hollow rings designate experiments during which decomposition of Ca_3SiO_5 occurred, the full rings represent non-decomposed Ca_3SiO_5 phase and the white-black rings indicate Ca_3SiO_5 in metastable state.

tion of C_3S , as proved by experiments Nos. 2, 3 and 4 (Table II) where tricalcium silicate was completely decomposed within several minutes.

The accelerating influence of pressure on the decomposition kinetics of C_3S at temperatures lower than 1525 K (lower thermal stability limit of C_3S) follows from the comparison of the high-pressure experiments (Table II, experiments Nos 5, 6) with the heating experiments carried out at normal pressure (Table I, experiments Nos. 1, 2). Whereas in the high-temperature experiments at normal pressure the first traces of decomposition phases appeared first after 30 minutes of heating, under combined effects of pressure the decomposition of tricalcium silicate occurred

Table II

The effect of pressure on stability of Ca_3SiO_5 at high temperatures

No.	$\frac{P_{max}}{GPa}$	$\frac{\tau P_{max}}{min}$	Heating cycles	$\frac{T_{max}}{K}$	$\frac{\tau T_{max}}{min}$	Degree of Ca_3SiO_5 decomposition $\alpha/mole\%$	Decomposition products
1.	1.0	20	1	770	1	0	—
2.	1.0	20	1	1770	1	100	$\beta-Ca_2SiO_4 + CaO$
3.	3.5	50	1	1620	15	100	$\beta-Ca_2SiO_4 + CaO$
			2	1620	5		
4.	4.5	50	1	1670	15	100	$\beta-Ca_2SiO_4 + CaO$
			2	1670	5		
5.	6.0	60	1	1170	10	100	$\beta-Ca_2SiO_4 + CaO$
			2	1170	10		
			3	1170	5		
6.	6.5	50	1	1270	20	100	$\beta-Ca_2SiO_4 + CaO$
7.	7.3	20	—	293	—	0	—
8.	8.3	60 days	—	293	—	0	—

P_{max} = maximum pressure; τP_{max} = time of effect of maximum pressure;
 T_{max} = maximum temperature; τT_{max} = time of effect of maximum temperature.

within several minutes. At the temperatures close to the lower limit of thermal stability of C_3S , the first traces of decomposition phases at normal pressure appeared only after several tens of hours (Table I, experiment No. 2). At lower temperatures, even the effect of high pressure did not succeed in decomposing C_3S (e.g. at 770 K and 1 GPa, Table II, experiment No. 1) as a result of the slow rate of the decomposing reaction in the lower temperature interval, which may also serve for fixing the metastable state of the compound.

The effect of pressure on the direction of reaction (1) is controlled by the condition of increasing density of reaction products under pressure compared to the density of phases entering the reaction.

At room temperature and under normal pressure, the density of C_3S , ρ_{C_3S} , calculated from the relative molar weight ($M = 228.323$) and from the weighed mean of experimentally determined volumes of the unit cells of type T_1 tricalcium

silicate (triclinic form with reduced unit cell volume $V/Z = 121.05 \times 10^{-30} \text{ m}^3$ [6, 15, 19]) has the value $\rho_{\text{C}_3\text{S}}^{293} = 3.1314 \text{ Mg/m}^3$. The density of CaO ($M = 56.0784$, $V/Z = 27.83 \times 10^{-30} \text{ m}^3$ [20]) is $\rho_{\text{CaO}}^{293} = 3.3454 \text{ Mg/m}^3$. The density of Ca_2SiO_4 depends on the respective modification. For the γ -form, the density value $\rho_{\gamma\text{-Ca}_2\text{SiO}_4}^{293} = 2.9865 \text{ Mg/m}^3$ ($M = 172.2436$, $V/Z = 96.75 \times 10^{-30} \text{ m}^3$ [21–25]), $\rho_{\beta\text{-Ca}_2\text{SiO}_4}^{293} = 3.3116 \text{ Mg/m}^3$ ($V/Z = 86.35 \times 10^{-30} \text{ m}^3$ [24–31]), $\rho_{\alpha'\text{-Ca}_2\text{SiO}_4}^{293 \text{ stab.}} = 3.3418 \text{ Mg/m}^3$ ($V/Z = 85.57 \times 10^{-30} \text{ m}^3$ [21, 32, 33]). At the lower limit of the thermal stability of C_3S (1525 K) and under normal pressure, $\rho_{\text{C}_3\text{S}}^{1525} = 2.9980 \text{ Mg/m}^3$ ($V/Z = 126.43 \times 10^{-30} \text{ m}^3$ [19]) $\rho_{\alpha'\text{-Ca}_2\text{SiO}_4}^{1552} = 3.0941$ ($V/Z = 92.42 \times 10^{-30} \text{ m}^3$ [34]), $\rho_{\text{CaO}}^{1525} = 3.1872 \text{ Mg/m}^3$ ($V/Z = 29.21 \times 10^{-30} \text{ m}^3$ [35]). At higher temperatures, the densities of C_3S and of α' - Ca_2SiO_4 tend to become equal as a result of the higher thermoexpansion coefficient of the α' -form [34]. Formation of the γ -form of dicalcium silicate during decomposition of C_3S at high temperatures and under high pressures is improbable owing to the lower density of γ - Ca_2SiO_4 compared to that of C_3S . This conclusion is also confirmed by the pressure experiments with γ - Ca_2SiO_4 . The experimental results are summarized in Table III. These imply that under high pressures and at high temperatures the γ -form was always transformed to the β -form. The proportions of phases γ and β changed in dependence on the values P , T and on the time of the effect of pressure and temperature.

Table III

The effect of pressure on polymorphous transformation of γ - Ca_2SiO_4 at high temperatures. The significance of symbols P_{max} , T_{max} and τ is the same as that in Table II

No.	$\frac{P_{\text{max}}}{\text{GPa}}$	$\frac{\tau P_{\text{max}}}{\text{min}}$	Heating cycles	$\frac{T_{\text{max}}}{\text{K}}$	$\frac{\tau T_{\text{max}}}{\text{min}}$	Content of β - Ca_2SiO_4
						$\frac{c}{\text{mole \%}}$
1.	6.0	50	1	1170	10	50–60
			2	1170	10	
			3	1170	10	
2.	5.8	60	1	640	0.17	85–95
			2	739	0.5	
			3	777	1.0	
			4	987	0.5	
			5	939	0.17	
3.	4.5	70	—	293	—	40–50

The lowest content of the transformed β -form resulted from the high-pressure experiment at room temperature (Table III, experiment No. 3). The high-pressure experiments carried out at temperatures above 1000 K up to pressures of 1 GPa yielded as the primary product the α' -form of dicalcium silicate which, however, transformed reversibly to β -form on cooling down [36]. In view of the fact that the cooling down was performed under high pressure, which exceeded the value of the equilibrium pressure of the stability region of β -form, the decompression probably did not lead to any transformation of the β -form to the stable γ -form. The proportion of γ -form identified by X-ray powder diffraction analysis in conclusion of the experiment probably represents the nontransformed portion of the original γ -form. In the products of decomposition of C_3S under high pressure

and high temperature (Table II) the X-ray diffraction analysis identified as the main phases β -Ca₂SiO₄ and CaO, whereas the γ -form was present in traces only. A stabilizing effect of CaO on β -Ca₂SiO₄ cannot likewise be ruled out.

An even more general view of the high-pressure transformation of C₃S is provided by the structural field theory [37, 38] which relates the phase and modification transformations under high pressures and at high temperatures with the so-called coefficient of packing, Φ . This coefficient is given by the ratio of volume V_a , taken up by atoms in the unit cell, to the volume V of the unit cell:

$$\Phi = \frac{V_a}{V}. \tag{1}$$

On the assumption of a spherical symmetry of ions, equation (1) can be written in the form

$$\Phi = \frac{\frac{4}{3} \pi \sum_i r_i^3}{V}, \tag{2}$$

where r_i are ionic radii of atoms in the unit cell, where the coordination number of atoms and the overlap of the electron envelopes of oxygen atoms in tetrahedral groups SiO₄ has also to be taken into account [38]. Table IV lists the composition,

Table IV

Structural data on the compounds Ca₃SiO₅, α' -Ca₂SiO₄, β -Ca₂SiO₄, γ -Ca₂SiO₄, CaO: structural type, coordination formula, symmetry, volume of atoms in the unit cell V_a , reduced volume of unit cell V/Z , coefficient of packing Φ , calculated density ρ_x

Compound	Ca ₃ SiO ₅	α' -Ca ₂ SiO ₄
Structural type	Ca ₃ SiO ₅	β -K ₂ SO ₄
Coordination formula	VII _{Ca6} VI _{Ca46} IV _{Si18} VI _{O18} VO ₉ IV _{O66}	IX _{Ca} VII _{Ca} IV _{Si} V _{O6}
Symmetry	triclinic	orthorhombic
$\frac{V_a}{Z} / 10^{-30} \text{ m}^3$	1230.25	56.94
$\frac{V}{Z} / 10^{-30} \text{ m}^3$	2178.90/18	85.57
Φ	0.565	0.665
$\rho_x / \text{Mg m}^{-3}$	3.1314	3.3418

Compound	β -Ca ₂ SiO ₄	γ -Ca ₂ SiO ₄	CaO
Structural type	deformed β -K ₂ SO ₄	olivine	NaCl
Coordination formula	VIII _{Ca} VII _{Ca} IV _{Si} VO ₅ IV _O	VI _{Ca5} IV _{Si} IV _{O4}	VI _{Ca} VI _O
Symmetry	monoclinic	orthorhombic	cubic
$\frac{V_a}{Z} / 10^{-30} \text{ m}^3$	55.70	52.40	15.68
$\frac{V}{Z} / 10^{-30} \text{ m}^3$	86.35	96.75	27.83
Φ	0.645	0.542	0.564
$\rho_x / \text{Mg m}^{-3}$	3.3116	2.9865	3.3454

structural type, values of volumes V_0 , reduced volumes of elementary cells V/Z at room temperature and under normal pressure, and the respective coefficients of packing Φ for C_3S , γ -, α' -, β - Ca_2SiO_4 and CaO . The values of ionic radii published by Shannon were used in the calculation [39]. Table IV indicates that whereas C_3S and CaO have comparable values of the coefficient of packing ($\Phi_{C_3S} = 0.565$, $\Phi_{CaO} = 0.564$), β - Ca_2SiO_4 and α' - Ca_2SiO_4 have higher values of the Φ coefficients ($\Phi_{\beta-Ca_2SiO_4} = 0.645$, $\Phi_{\alpha'-Ca_2SiO_4} = 0.665$). As the Φ for γ - Ca_2SiO_4 is significantly lower than that for C_3S ($\Phi_{\gamma-Ca_2SiO_4} = 0.542$), any pressure transformation of C_3S to $CaO + Ca_2SiO_4$ would be improbable, if the γ -form of dicalcium silicate would have to be formed.

Calculation of the stability region of C_3S in the P - T diagram

The following equation was used in the calculation of the equilibrium pressure and temperature at which the C_3S , Ca_2SiO_4 and CaO phases co-exist:

$$\Delta G_{eq} - \Delta G^\circ = \int_{P_n}^{P_{eq}} \Delta V dP. \quad (3)$$

Under equilibrium conditions, the change in Gibbs energy ΔG_{eq} is equal to zero. ΔG° is a standard change in Gibbs energy at temperature T under normal pressure P_n ($P_n = 1.0133 \times 10^5$ Pa), P_{eq} is the pressure of the equilibrium transformation and ΔV is the volume change due to reaction (1). Table V lists the volume changes of CaO and various modifications of C_3S and Ca_2SiO_4 in terms of temperature.

Table V

Molar volumes V_M of phases Ca_3SiO_5 , Ca_2SiO_4 and CaO at temperatures T and under normal pressure

Compound	Modification	Temperature	Molar volume
		$\frac{T}{K}$	$\frac{V_M}{10^{-6} \text{ m}^3 \text{ mole}^{-1}}$
Ca_3SiO_5	T ^I	298	72.908
	R	1315	75.378
	R	1400	75.655
	R	1500	76.035
	R	1600	76.455
	R	1693	76.640
Ca_2SiO_4	α' — stabilized	298	51.539
	$\alpha'L$	1315	54.719
	$\alpha'L$	1400	55.101
	$\alpha'H$	1500	55.333
	$\alpha'H$	1600	55.498
	$\alpha'H$	1693	55.652
CaO		298	16.762
		1315	17.473
		1400	17.531
		1500	17.599
		1600	17.667
		1693	17.731

Table VI

Thermodynamic data for the decomposition reaction of Ca_3SiO_5 in solid state

Temperature $\frac{T}{\text{K}}$	Modification of Ca_2SiO_4	$\frac{\Delta H_T^\circ}{\text{J mole}^{-1}}$	$\frac{\Delta G_T^\circ}{\text{J mole}^{-1}}$	$\frac{P_{\text{eq}}}{\text{GPa}}$
298	γ	-10 467	-7 972	
300	γ	-10 450	-7 955	
400	γ	-10 253	-7 189	
500	γ	-10 739	-6 368	
600	γ	-11 313	-5 439	
700	γ	-11 719	-4 425	
800	γ	-11 832	-3 375	
900	γ	-11 581	-2 324	
1 000	$\alpha'L$	-7 042	-1 562	
1 100	$\alpha'L$	-7 298	-1 000	
1 200	$\alpha'L$	-7 469	-415	
1 300	$\alpha'L$	-7 566	-176	
1 315	$\alpha'L$	-7 567	0	normal
1 400	$\alpha'H$	-7 574	775	0.256
1 500	$\alpha'H$	-7 503	1 365	0.440
1 600	$\alpha'H$	-7 344	1 951	0.593
1 693	$\alpha'H$	-7 126	2 525	0.775

Table VI summarizes the thermodynamical data for the decomposition of C_3S , evaluated by means of thermodynamic tables [40]. ΔH_T° and ΔG_T° are standard changes in enthalpy and Gibbs energy of reaction (1) respectively at temperature T , and P_{eq} is the equilibrium pressure at temperature T , for the evaluation of which is possible to use equation (3). It was further assumed that in the region of pressures of up to about 0.8 GPa, compressibility does not yet influence the volume change ΔV , evaluated by means of the data in Table V for reaction (1), proceeding in solid phase at temperature T and under normal pressure P_n . In other words, compressibility of phases C_3S , Ca_2SiO_4 and CaO was assumed to be approximately identical up to pressures of about 0.8 GPa.

The value of equilibrium temperature T_{eq} under normal pressure is 1315 K (Table VI). This value is somewhat lower than the experimentally established stability limit of C_3S (1525 K), but higher than the equilibrium temperature calculated by Berezhnoy (1248 K, [3]). It is impossible to assess to what extent the difference between the equilibrium temperature suggested in the present study and the experimentally established value is significant, because the thermodynamic data [40] used in the calculation of data in Table VI were published without any information on measuring errors. In Fig. 1, the stability limit of C_3S is indicated by points (P_{eq}, T) , the parameters of which are specified in Table VI. The slope of the limit was verified by means of Clausius-Clapeyron equation adjusted for evaluation of reaction (1):

$$\frac{dT}{dP} = \frac{\Delta V_{\text{eq}} T}{\Delta H_{\text{eq}}} \quad (4)$$

For pressures close to the normal pressure, the values of the slope dT/dP are obtained on substituting the following data: $T = 1315$ K, $\Delta H_{\text{eq}} = -7567$ J/mole, $\Delta V_{\text{eq}} = -3.19 \times 10^{-6}$ m³/mole. The slope $dT/dP = 550$ K/GPa, calculated by means of equation (4), passes approximately through points P_{eq} , T evaluated by means of equation (3). This implies that the assumptions used in the processing of thermodynamic data [40] by means of equations (3) and (4) were correct. If we were to accept the value on equilibrium temperature under normal pressure ($T = 1525$ K) obtained experimentally, as a more justified one, the stability limit of C_3S would then represent, in the lower pressure region, the line passing from point $T = 1525$ K, $P_{\text{eq}} = 1.0133 \times 10^5$ Pa (normal pressure) with a slope of 550 K/GPa (full line in Fig. 2).

The comparatively wide region of C_3S metastability is further confirmed by experiments Nos. 7 and 8 (Table II), where for instance the X-ray experiment No 8 was carried out "in situ", and no decomposition of C_3S occurred during 2-months of compression under extreme pressure and at room temperature (Fig. 1).

CONCLUSION

Using the condition for the equilibrium of solid phase reaction and by means of Clausius - Clapeyron equation, the stability limit of C_3S was investigated in the P - T diagram in the region of pressures up to 0.8 GPa. Under the effect of pressure, the equilibrium temperature of reaction $Ca_3SiO_5 \rightleftharpoons Ca_2SiO_4 + CaO$ is shifted towards the higher temperature region at a slope $\Delta T/\Delta P = 550$ K GPa⁻¹. This means that a change in the direction of the reaction can be achieved in the temperature range where synthesis of C_3S takes place under normal pressure. Dicalcium silicate, which results from the decomposition of C_3S according to the pressure and temperature values, is only capable of crystallizing in the form of β - Ca_2SiO_4 , or α' - Ca_2SiO_4 , which is converted to β -form on cooling down under pressure. In agreement with the structure field theory as well as with experiments, formation of γ - Ca_2SiO_4 is improbable. At lower temperatures and pressures, e.g. at 770 K and 1 GPa, and likewise under extreme pressures at room temperature, C_3S is no longer decomposed owing to the slower kinetics of reaction (1), and the metastable state of tricalcium silicate is retained.

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ВЛИЯНИЕ ДАВЛЕНИЯ И ТЕМПЕРАТУРЫ НА ФАЗОВУЮ УСТОЙЧИВОСТЬ ТРИКАЛЬЦИЙСИЛИКАТА

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С помощью условия для равновесия реакции в твердой фазе и уравнения Клауснуса—Клапейрона рассмотрели нижний предел устойчивости Ca_3SiO_5 в P — T диаграмме в области давлений до 0,8 ГПа с уклоном $\Delta T/\Delta P = 550 \text{ ГПа}^{-1}$. Устойчивость и метастойчивость Ca_3SiO_5 экспериментальным путем исследовали при давлениях до 8 ГПа и температурах до 1800 К. Экспериментальным путем было доказано, что действием давления можно достичь в области температур, когда происходит при нормальном давлении синтез Ca_3SiO_5 , изменения направления и кинетики реакции.

Теоретически и экспериментальным путем было доказано, что дикальцийсиликат, образующийся при распаде Ca_3SiO_5 , в зависимости от величины используемых давлений и температур, может кристаллизоваться только в виде β — или α' - Ca_2SiO_4 , конвертирующего при охлаждении под давлением в β -форму.

Рис. 1. Пределы устойчивости Ca_3SiO_5 в P — T диаграмме. Точки (+) ограничивают

поле устойчивости Ca_3SiO_5 с помощью равновесного уравнения (3). Уклон штриховой прямой, проходящей через точки (+) представляет собой дифференциальное частное dT/dP , установленное с помощью уравнения (4). Сплошная линия,

параллельная с уклоном dT/dP , исходит из пункта $T_{eq} = 1525$ К, P_{eq} = нормальное давление, который был установлен экспериментальным путем. Полные кружки обозначают эксперименты, при которых происходило разложение Ca_3SiO_5 , полные кружки обозначают неразложившуюся фазу Ca_3SiO_5 и бело-черные кружки — Ca_3SiO_5 в метастабильном состоянии.

VPLYV TLAKU A TEPLoty NA FÁZOVÚ STABILITU TRIKALCIUMSILIKÁTU

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Pomocou podmienky pre rovnováhu reakcie v tuhej fáze a pomocou Clausius — Clapeyronovej rovnice sa vyhodnotila dolná hranica stability Ca_3SiO_5 v P - T diagrame v oblasti tlakov do 0.8 GPa so sklonom $\Delta T/\Delta P = 550$ GPa⁻¹. Stabilita i metastabilita Ca_3SiO_5 sa experimentálne vyšetrovala pri tlakoch do 0.8 GPa a teplotách do 1800 K. Experimentálne sa dokázalo, že účinkom tlaku je možno dosiahnuť v oblasti teplôt, kedy dochádza za normálneho tlaku k syntéze Ca_3SiO_5 , zmenu smeru a kinetiky reakcie.

Teoreticky i experimentálne sa dokázalo, že dikalciumsilikát, ktorý vzniká pri rozklade Ca_3SiO_5 , v závislosti na hodnote použitého tlaku a teploty, môže kryštalizovať len vo forme β - alebo α' - Ca_2SiO_4 , konvertujúci pri ochladení za tlaku na β -formu.

Obr. 1. Hranica stability Ca_3SiO_5 v P — T diagrame. Body (+) ohraničujú pole stability Ca_3SiO_5 pomocou rovnovážnej podmienky (3). Sklon čiarkovanej priamky, prechádzajúcej bodmi (+), je diferenciálny kvocient dT/dP , určený pomocou rovnice (4). Plná čiara, rovnobežná so smernicou dT/dP , vychádza z bodu $T_{eg} = 1525$ K, P_{eg} = normálny tlak, ktorý bol zistený experimentálne. Prázdne krúžky označujú experimenty, pri ktorých nastal rozklad Ca_3SiO_5 , plné krúžky reprezentujú nerozloženú fázu Ca_3SiO_5 a bielo-čierne krúžky Ca_3SiO_5 v metastabilnom stave.