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SHORT COMMUNICATIONS

Rutile–Quartz Geothermobarometer

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INTRODUCTION

The system quartz with dissolved TiO_2–rutile is of particular interest for geochemistry. Several authors [1–4] described bluish quartz grains with rutile needles from the granulites, charnockites, and gneisses of shield regions. Rutile in quartz was considered as an exsolution product formed under decreasing temperature from the $(Si,Ti)O_2$ solid solution [2, 4, 5]. Our previous study [6] of quartz samples hydrothermally synthesized at a pressure of 200 MPa and various temperatures showed that the content of TiO_2 in the quenched quartz phase $(Si, Ti)O_2$ (i.e., in α-quartz formed after β-quartz with dissolved TiO_2) is not high: ~0.1 wt % TiO_2 at 900°C and 0.3 wt % TiO_2 at 1000°C according to electron microprobe analysis. Samples from 550 and 750°C experiments could not be analyzed with an electron microprobe because of their low TiO_2 content and the small sizes of quartz grains. However, it was shown that the TiO_2 content of quartz can be independently determined by means of precise measurements of the unit cell parameters *a* and *c* of quartz [6] using the autocorrection method developed by Gamarnik [7]. The mechanism of the incorporation of titanium admixture into the quartz lattice was evaluated on the basis of both variations in the unit-cell parameters (*a* and *c*) of the synthetic samples [6] and the investigation of their spectroscopic properties (luminescence spectra, diffuse reflection, and electron paramagnetic resonance [8]). These data showed that titanium is incorporated into the quartz structure as tetravalent ions and most of them isomorphically substitute for silicon ions. In this paper, the data of [6] are used to obtain the *P–T–X* curves of the $(Si, Ti)O_2$ (quartz phase)–TiO_2 (rutile) equilibrium, which are a common form of geothermometers and geobarometers. These curves are compared with a variant of the rutile–quartz geothermometer (at a pressure of 200 MPa) proposed by Kurepin [9]. It was also shown that the TiO_2 content of quartz synthesized at 340°C and ~1 kbar is very low.

EXPERIMENTAL RESULTS AND DISCUSSION

Among the two aforementioned microprobe determinations of TiO_2 content in samples from the 900 and 1000°C experiments (at 200 MPa), the most reliable is definitely the average value obtained for three samples from the 1000°C experiments. The average for 21 quartz grains is 0.33 ± 0.9 wt %, which corresponds to the mole fraction $X_{TiO_2} = (2.48 \pm 0.66) \times 10^{-3}$.

It was shown in [6] that the volume (V) of the $(Si, Ti)O_2$ quartz phase increases almost linearly with increasing X_{TiO_2}, which indicates that the isomorphic substitution of Ti^{4+} for Si^{4+} complies with Vegard's rule. Correspondingly, linear relationships were observed for the relative increments of the unit-cell parameters *a* and *c* and volume *V*. In particular,

$$\Delta V/V = \alpha X_{TiO_2}, \qquad (1)$$

where the coefficient α can be determined from the values of $\Delta V/V$ and X_{TiO_2} at 1000°C: $\alpha = (\Delta V/V)/X_{TiO_2} = 0.258$.

Using this α value and $\Delta V/V$ for temperatures of 900, 750, and 550°C (3.4×10^{-4}, 1.7×10^{-4}, and 0.4×10^{-4}, respectively), mole fractions and weight percentages of TiO_2 in the quartz phase can be obtained for these temperatures and a pressure of 200 MPa (Table 1). These "combined" values are in adequate agreement with the values of X_{TiO_2} and weight percent TiO_2 in the quartz phase derived on the basis of the precise measurements of unit-cell parameters [6].

The obtained weight concentrations of TiO_2 were used to construct temperature–composition curves for the equilibrium rutile–$(Si, Ti)O_2$ quartz phase at a pressure of 200 MPa (Fig. 1, curve 2). This curve is a rutile–quartz geothermometer at $P = 200$ MPa. The dashed line in Fig. 1 shows the rutile–quartz geothermometer ($P = 200$ MPa) proposed by Kurepin [9] on the basis of TiO_2 contents in quartz grains from the Berdichev granites (Ukrainian shield), which were formed under various temperatures (which were estimated using garnet–cordierite and garnet–biotite thermometers). As can be seen, at a given TiO_2 concentration in the quartz phase, the Kurepin geothermometer [9] overestimates temperature by ~50°C at temperatures of 600–700°C and by ~100°C at 900–1000°C.

It is instructive to estimate the influence of pressure on the position of the rutile–quartz geothermometric curve. As was mentioned above, the incorporation of TiO_2 into the quartz phase results in a linear increase in its molar volume. Therefore, an increase in pressure must reduce the incorporation of Ti, i.e., must result in TiO_2 exsolution from the (Si, Ti)O_2 phase under a given temperature. The value of $X_{\mathrm{TiO_2}}$ will decrease with increasing pressure at a given temperature. The curves of $TX_{\mathrm{TiO_2}}$ for various pressures can be obtained from the 200 MPa $TX_{\mathrm{TiO_2}}$ curve, the molar volume of rutile (V_{ru}), and the partial molar volume of the TiO_2 component ($\bar{V}_{\mathrm{TiO_2}}$) in the quartz phase. Using the thermodynamic equation

$$(\partial \ln X_{\mathrm{TiO_2}}/\partial P)_T = (V_{\mathrm{ru}} - \bar{V}_{\mathrm{TiO_2}})/RT \tag{2}$$

an expression can be obtained for the calculation of $X_{\mathrm{TiO_2}}$ assuming that V_{ru} and $\bar{V}_{\mathrm{TiO_2}}$) are practically independent of pressure:

$$X^{P}_{\mathrm{TiO_2}} = X^{P_0}_{\mathrm{TiO_2}} \exp[(V_{\mathrm{ru}} - \bar{V}_{\mathrm{TiO_2}})/RT](P - P_0), \tag{3}$$

where $X^{P}_{\mathrm{TiO_2}}$ and $X^{P_0}_{\mathrm{TiO_2}}$ are the $X_{\mathrm{TiO_2}}$ values at pressure P and the initial pressure P_0 = 200 MPa, respectively.

The partial molar volumes of the TiO_2 component ($\bar{V}_{\mathrm{TiO_2}}$) in the quartz phase were determined at 20, 900, and 1000°C taking into account thermal expansion [10, 6]. Similar estimates were obtained for temperatures of 550 and 750°C. The following $\bar{V}_{\mathrm{TiO_2}}$ values were calculated for temperatures of 20, 550, 750, 900, and 1000°C: 28.13, 29.28, 29.33, 29.36, and 29.34 cm^3/mol, respectively. As can be seen, the obtained values are practically identical starting from 550°C. The values of V_{ru} for the same temperatures are 18.80, 19.08, 19.15, 19.24, and 19.30 cm^3/mol, respectively. Using $X_{\mathrm{TiO_2}}$ at P = 200 MPa (Table 1) and the obtained V_{ru} and $\bar{V}_{\mathrm{TiO_2}}$) values, $X_{\mathrm{TiO_2}}$ can be calculated for pressures of 400, 600, 800, 1000, and 100 MPa (Table 2). The contents of TiO_2 in weight percent were calculated from these $X_{\mathrm{TiO_2}}$ values and are shown in Fig. 1. Equilibrium temperature–composition curves are drawn through these points for pressures of 100, 400, 600, 800, and 1000 MPa (curves 1 and 3–6, respectively). The set of curves (1)–(6) in Fig. 1 can be considered as a rutile–quartz geothermobarometer. As can be seen, the content of TiO_2 in quartz increases significantly with increasing temperature and decreases with increasing pressure.

Table 1. TiO_2 content in the (Si, Ti)O_2 quartz phase at temperatures of 550, 750, 900, and 1000°C and P = 200 MPa

T, °C	TiO_2 in (Si, Ti)O_2 quartz phase	
	wt %	Mole fraction, $X_{\mathrm{TiO_2}}$
550	0.03	0.19×10^{-3}
750	0.09	0.66×10^{-3}
900	0.18	1.32×10^{-3}
1000	0.33	2.48×10^{-3}

Table 2. Mole fraction of TiO_2 ($X_{\mathrm{TiO_2}}$) in the (Si, Ti)O_2 quartz phase at various pressures and temperatures

P, MPa	550°C	750°C	900°C	1000°C
100	0.22×10^{-3}	0.74×10^{-3}	1.46×10^{-3}	2.73×10^{-3}
200	0.19×10^{-3}	0.66×10^{-3}	1.32×10^{-3}	2.48×10^{-3}
400	0.14×10^{-3}	0.51×10^{-3}	1.07×10^{-3}	2.05×10^{-3}
600	0.11×10^{-3}	0.41×10^{-3}	0.87×10^{-3}	1.69×10^{-3}
800	0.08×10^{-3}	0.33×10^{-3}	0.71×10^{-3}	1.40×10^{-3}
1000	0.06×10^{-3}	0.26×10^{-3}	0.57×10^{-3}	1.16×10^{-3}

The conditions of equilibrium for the curves shown in Fig. 1 can be expressed as

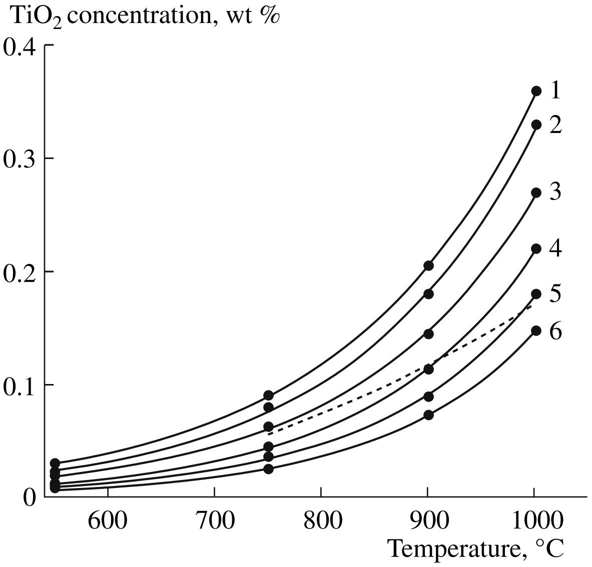

Fig. 1. Temperature (T) versus composition (wt %) curves for the equilibrium between rutile and (Si, Ti)O_2 quartz phase at various pressures (MPa): (1) 100, (2) 200, (3) 400, (4) 600, (5) 800, and (6) 1000.

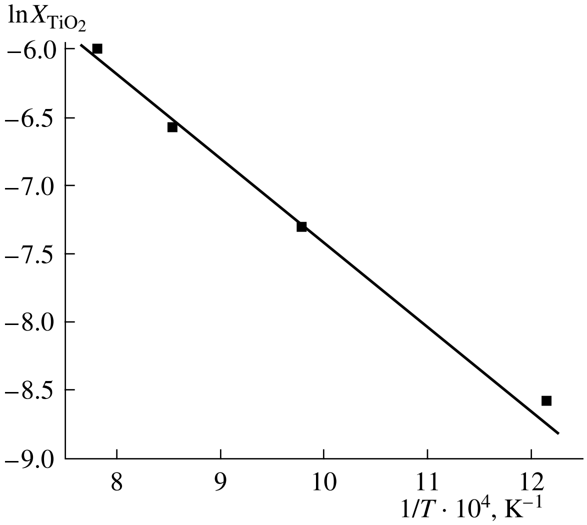

Fig. 2. Logarithm of TiO_2 mole fraction in the quartz phase as a function of reciprocal temperature at 200 MPa.

$$\Delta G^0(T, P) = -RT\ln a, \quad (4)$$

where $\Delta G^0(T, P)$ is the difference between the chemical potential of the TiO_2 component of the fictive end-member quartz phase consisting of TiO_2 and the chemical potential of rutile, and a is the activity of the TiO_2 component in the (Si, Ti)O_2 quartz phase ($a = \gamma_{TiO_2} x_{TiO_2}$, where γ_{TiO_2} is the activity coefficient).

Assuming that the activity coefficient is almost temperature independent, Eq. (2) can be transformed into the well-known thermodynamic relation

$$(\partial \ln X_{TiO_2}/\partial T)_P = \Delta H^0/RT^2, \quad (5)$$

where ΔH^0 is the heat effect (at P = const) of TiO_2 incorporation into the quartz phase. If ΔH^0 is also practically temperature independent, the following common integral expression can be obtained:

$$\ln(X_{TiO_2}/X^0_{TiO_2}) = (\Delta H^0/R)(T - T_0)/T_0T, \quad (6)$$

where T_0 and $X^0_{TiO_2}$ are the arbitrary initial values of temperature and TiO_2 concentration in the quartz phase. As can be seen, $\ln X_{TiO_2}$ is a linear function of $1/T$.

Figure 2 shows the dependence of $\ln X_{TiO_2}$ on $1/T$ constructed on the basis of X_{TiO_2} values from Table 2. As can be seen, this relationship is nearly linear. The heat effect of TiO_2 dissolution in the (Si, Ti)O_2 quartz phase can be estimated from it as $\Delta H^0 = 12 \pm 2$ kcal/mol (or 50 ± 8 kJ/mol).

The curves of rutile–(Si, Ti)O_2quartz phase equilibrium (Fig. 1) suggest that the TiO_2 content of quartz becomes very low at temperatures below 500°C. In order to check this inference, small quartz monocrystals were experimentally grown on seeds of the base and small rhombohedron in an alkaline solution (4% NaOH) using the temperature difference method [11]. The growth was conducted in an autoclave (0.2 l in volume) at $T = 340°C$, a temperature difference of $\Delta T = 5°C$, and a pressure of 120 MPa. A container with rutile grains was placed in the dissolution zone together with a quartz charge. The thickness of newly grown quartz formed within 10 days was 3 mm on the base and 2 mm on the small rhombohedron. Microprobe analysis indicated the absence of TiO_2 in the newly grown layer. The spectral analysis of the newly grown quartz showed 0.006 wt % TiO_2. Similar concentrations were determined for Mn, Ni, and Cr, whereas those of Co, V, Nb, and Cu were an order of magnitude lower. The content of Fe was up to 0.1 wt %. These results suggest that TiO_2 is practically not accommodated in the quartz structure at such low temperatures.

Thus, the rutile–quartz geothermobarometer can be applied at high temperatures for the approximate estimation of the PT conditions of formation of quartz-bearing rocks. It is expedient to combine the investigation of the chemical composition of quartz with the precise determination of its unit-cell parameters, which is also important for the elucidation of the genesis of rutile crystals in quartz grains.

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