

Thermodynamics of mixing in rutile-stishovite solid solution from quantum-mechanical calculations

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The occurrence of Si-rich rutile (18 mol % of SiO₂) in a chromitite body within the ultra-high-pressure metamorphic sequence of Yarlungzangbu ophiolite in Southern Tibet (Yang et al. 2003) suggests that under certain conditions rutile forms a solid solution with stishovite. This opens the possibility of using the stishovite-coesite equilibrium for estimating pressures of crystallization of rocks containing coesite and rutile, since rutile can be treated as stishovite diluted with TiO₂. The association of rutile and coesite is typical for eclogite-type inclusions in diamonds (e.g. Kaminsky et al., 2000). The SiO₂ content of rutiles in coesite bearing rocks has yet not been studied systematically. A recent experimental study of Ren et al. (2005) showed, however, that at 10 GPa and 2073 K rutile in association with coesite dissolved about 2 mole % of SiO₂. This concentration level is detectable with a variety of analytical techniques. To calculate the rutile-coesite equilibrium as a function of pressure and temperature one needs the thermodynamic properties of pure coesite and stishovite and a model for the activity of stishovite in the stishovite-rutile solid solution:

$$\Delta G_{T,P}^{\text{Stish}} + RT \ln a_{\text{SiO}_2}^{\text{Stish}} = \Delta G_{T,P}^{\text{Coes}} \quad (1)$$

Here the thermodynamic mixing properties of the SiO₂-TiO₂ solid solution are modeled with the recently developed Double Defect Method (DDM) (Vinograd et al., 2008). The DDM is based on first principles calculations of the formation energies of supercell structures with single B- and A- and paired BB- and AA-type defects inserted at all possible distances in the supercells of A and B end-members. These energies are converted to the so-called pair interaction energies, J_n , with the equation

$$J_n = (2\Delta H_{\text{single}} - \Delta H_{\text{double}}^{(n)}) / D_n, \quad (2)$$

where ΔH_{single} and $\Delta H_{\text{double}}^{(n)}$ are the excess enthalpies of the structures with single and double defects and D_n is the degeneracy factor for the pair of defects at the n -th distance. These J_n values are further used to get an approximation for the excess enthalpy of any A_xB_(1-x) structure within the supercell using the equation

$$\Delta H_i = \sum_n f_{AB}^{(n)} J_n, \quad (3)$$

where $f_{AB}^{(n)}$ is the frequency of pairs of AB-type at the n -th distance within the supercell. Such an

approximation makes it possible to use a Monte Carlo algorithm to calculate temperature dependent enthalpies of mixing within a much bigger supercell, where thermodynamic properties approach those of a real crystal. The Gibbs free energies of mixing and the thermodynamic activities can then be calculated from the temperature-dependent enthalpies with the thermodynamic integration method (Warren et al., 2001).

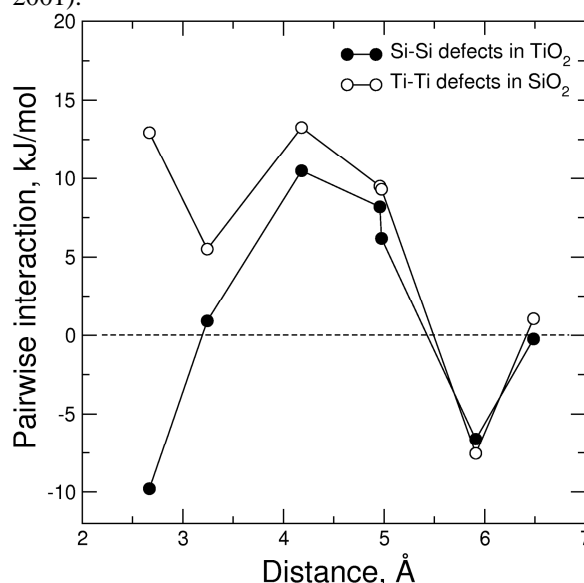


Fig. 1. The effective pair interactions, the J_n s, at 3 GPa in the stishovite-rutile solid solution calculated with the DDM. Positive sign corresponds to the clustering tendency.

In this study we have considered $2 \times 2 \times 3$ supercells of $P4/mnm$ stishovite and rutile with the parameters ($a = 8.3602$ Å and $c = 8.004$ Å). The size of these supercells permits consideration of seven SiSi- and TiTi-type defects in rutile and stishovite, respectively, located at different distances within the range of 2.7–6.5 Å. The total energies of the end-members and of the structures with the double defects were calculated with the density functional theory (DFT) with the PBE exchange-correlation functional. The calculations were performed with the CASTEP code (Clark et al., 2005) at the Centre for Scientific Computing at the University of Frankfurt. The calculation used a plane-wave basis set cut-off of 380 eV and a $4 \times 4 \times 4$ Monkhorst-Pack grid of k-points. Ultrasoft pseudopotentials (Kresse and Hafner, 1994) were used to represent the effective non-local potential due to the nucleus and core-electrons. These settings permitted the total energy to be determined with an accuracy of 0.01 eV per supercell. The results of these calculations at the pressures of 3 and 8 GPa are listed in Table 1 and plotted in Figure 1.

Table 1 shows that the excess energies of both SiSi and TiTi defects are large and positive. This means that the solid solution has a strong tendency to phase separate. However, the excess energies of the SiSi defects are significantly smaller than those of the TiTi defects. This suggests that a certain range of Si-substitution is possible at the rutile side. It is also clear that the mixing effects are insensitive to pressure changes in the range of 3-8 GPa.

Table 1. The excess energies of single and double defect structures (in eV per supercell) in rutile and stishovite: 2×2×3 supercell, 24 exchangeable sites.

Single defects					
3 GPa			8 GPa		
Si	Ti		Si	Ti	
0.64	1.27		0.63	1.27	

Double defects					
Dist., Å	D_n	3 GPa		8 GPa	
		SiSi	TiTi	SiSi	TiTi
2.67	1	1.42	2.36	1.41	2.33
3.24	1	1.30	2.38	1.29	2.37
4.18	2	1.10	2.22	1.07	2.20
4.96	2	1.15	2.30	1.12	2.28
4.97	2	1.19	2.30	1.17	2.29
5.91	4	1.59	2.81	1.60	2.82
6.49	4	1.33	2.45	1.33	2.43

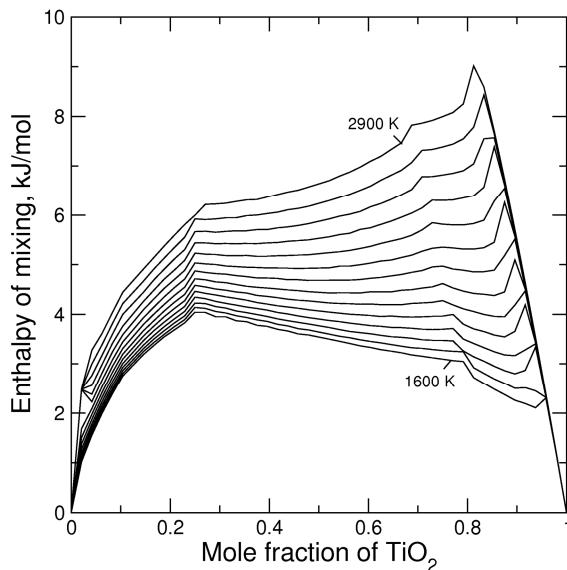


Fig. 2. The isotherms of the enthalpy of mixing in the rutile-stishovite solid solution from Monte Carlo simulations.

Figure 1 further shows that the pair interaction energies which correspond to SiSi defects in rutile are negative at the shortest distance, what means that such defects would tend to dissociate within the rutile structure, forming Si-Ti pairs and thus favouring mixing.

The J_n at intermediate compositions were linearly interpolated between the values which correspond to SiSi and TiTi defects. The combination of the effective pair interactions according to Equation 3 permits thus evaluation of the excess enthalpy of any configuration in the supercell. This equation was further used within

a Monte Carlo algorithm to calculate the temperature dependent enthalpies of mixing. Monte Carlo simulations were performed with a 12×12×12 supercell containing 5184 exchangeable sites. The calculations were done in the temperature range of 1600-2900 K with steps of 100 K and 0.02083 in the temperature and composition, respectively. The averages were calculated over the last half of $6 \cdot 10^7$ Monte Carlo steps. The calculated temperature-dependent enthalpies and the free energies are shown in Figures 2 and 3, respectively. Figure 3 shows that the mixing is restricted to Ti-rich compositions. The SiO₂ concentration in rutile in coexistence with stishovite progressively increases with the temperature and reaches about 10 mol % at 2900 K. The nearly flat segments in the enthalpy of mixing isotherms in Fig. 2 are a consequence of the phase separation which occurred in the course of the Monte Carlo simulations. It is observed that the enthalpy of mixing isotherms at the diluted concentrations follow the ideal mixing regime. This becomes apparent by comparing the enthalpy and the entropy isotherms, (Fig. 4). The ideal mixing becomes favourable due to the very strong tendency to phase separation which leads to the formation of the two phases with the Si- and Ti-rich compositions. The minorities of Si and Ti atoms are dispersed within the Ti- and Si-rich matrixes producing large entropy.

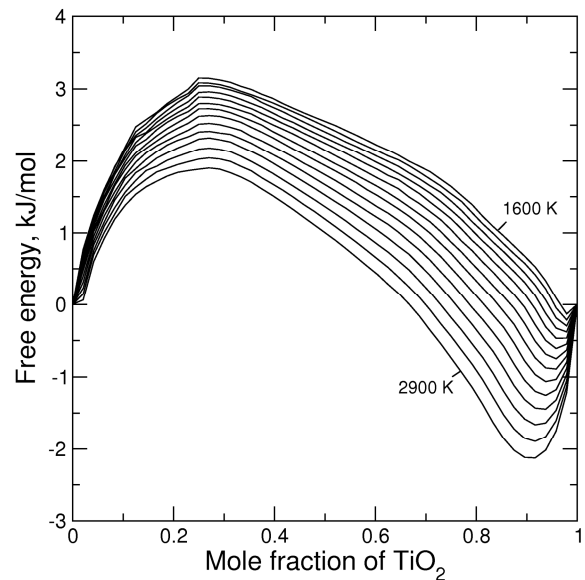


Fig. 3. The free energy of mixing calculated from the Monte Carlo results with the method of thermodynamic integration.

The excess free energies of mixing were fitted with the Redlich-Kister polynomial

$$G_{\text{excess}} = x_1 x_2 \sum_{i=1}^n (A_i + B_i T + C_i T^2) (x_2 - x_1)^i, \quad (4)$$

where x_1 and x_2 are the mole fractions of stishovite and rutile. The values of A , B and C coefficients are listed in Table 2.

Table 2. The parameters of the Redlich-Kister polynomial for the excess free energy in the stishovite-rutile solid solution

n	A_n (kJ)	$B_n \cdot 10^3$ (kJ/K/mol)	$C_n \cdot 10^6$ (kJ/K ² /mol)
0	9.95	25.99	1.70
1	-11.36	6.66	2.08
2	1.16	17.56	3.83
3	3.35	-4.78	1.14
4	12.27	3.31	3.13

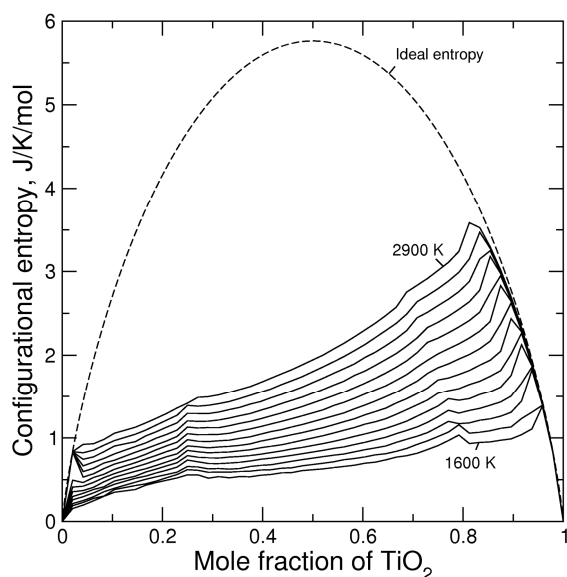


Fig. 4. The configurational entropy calculated with the equation $S=(H-G)/T$ using the calculated enthalpies and the free energies of mixing.

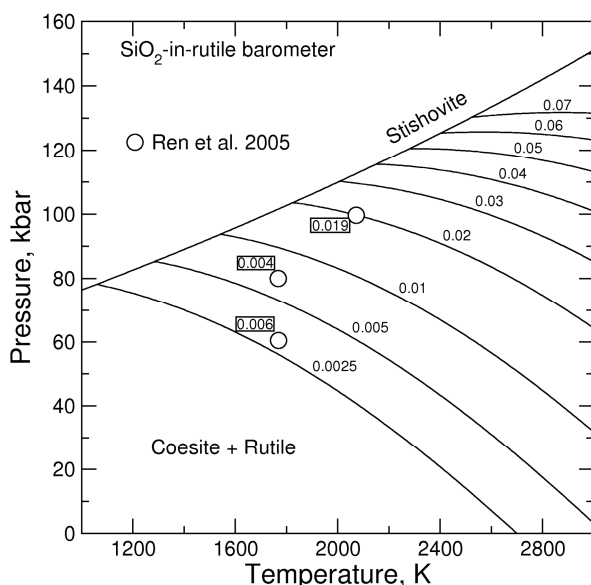


Fig. 5. The isopleths of SiO_2 mole fraction in rutile in equilibrium with coesite predicted using the presently derived activity-composition model. The experimental results of Ren et al. (2005) are also shown. The thermodynamic properties of coesite and stishovite are from the data base of Holland and Powell (1998).

The derived activities of the SiO_2 component were used to calculate the stishovite(rutile)-coesite equilibrium. The isopleths of SiO_2 concentration in

rutile in equilibrium with coesite (Fig. 5) are cut with the coesite/stishovite transition boundary where rutiles become saturated with SiO_2 ($a_{\text{SiO}_2}=1$). Our results are in good agreement with the experimental data of Ren et al. (2005).

Our calculations predict that the Si-in-rutile barometry would be very efficient at temperatures higher than 2000 K, where the Si-concentrations reach first mole %. For lower temperatures, a very sensitive local analytical technique would be needed. The method relies on the assumption that coesite is a pure phase and is applicable only in the cases where rutiles have not been transformed into the high pressure αPbO_2 -type structure. Further studies of the thermodynamics of SiO_2 - TiO_2 mixing in coesite and αPbO_2 structures would be useful to clarify possible errors due to violations of these assumptions.

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