Silicon self-diffusion in stishovite: calculations of point defect parameters based on the $cB\Omega$ thermodynamic model

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Abstract: We apply the $cB\Omega$ thermodynamic model to study the diffusion of Si in stishovite crystal at high-P and over a wide temperature range. According to this model, the point defect activation Gibbs free energy is expressed as a function of the bulk properties of the material, i.e. $g^{act}=cB\Omega$, where B is the isothermal bulk modulus, Ω is the mean atomic volume and c is a dimensionless constant. In this way, important point defect parameters, such as the activation volume v^{act}, the activation entropy s^{act} and the activation enthalpy h^{act} may be estimated, if the thermoelastic properties of the material are known over a wide temperature and pressure range. Our calculations are based on the EOS of stishovite, proposed by Wang et al. and on previously reported self-diffusion coefficients in stishovite single crystals measured at 14 GPa and at temperatures from 1400 to 1800 ^{o}C, in the [110] and [001] directions. Our results suggest that the point defect parameters exhibit considerable temperature dependence over the studied temperature range (1000-2000 ^{o}C). The estimated activation volumes (4.4-5.3 cm^3/mol, in the range 1400-1800 ^{o}C) are in agreement with the reported experimental results.

Keywords: *stishovite; self-diffusion; thermodynamic modelling; high-T; high-P; activation enthalpy; activation volume.*

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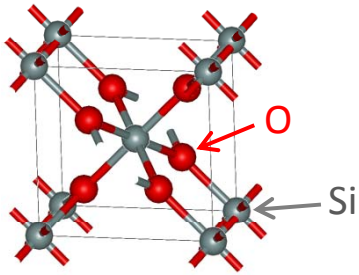
Motivation



- ✓ Stishovite plays a key role as a potential mineral that stores water in its crystal structure and transports it into the mantle.
- ✓ Appearance of stishovite in SiO_2-rich fragments may explain the presence of seismic reflectors in the mid-mantle region. Seismic reflectors would be affected by the rheological properties of the related materials undergoing plastic deformation under mantle conditions. Plastic deformation occurs either by diffusion or dislocation creep which are both controlled by ***atomic diffusion***.
- ✓ Silicon self-diffusion in stishovite was studied for the first time by Shatskiy et al. (2010) at the temperature range, 1400-1800 ^{o}C and at 14 Gpa.
- ✓ Important point defect parameters of Si diffusion in stishovite can be calculated on the basis of the ***cBΩ thermodynamic model***.

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The *cBΩ* thermodynamic model

The *cBΩ* model connects the point defect thermodynamic properties with the thermoelastic properties of the host material.

- ***Activation Gibbs free energy***: $g^{act} = c^{act} B \Omega$
  - B: isothermal bulk modulus
  - Ω: mean atomic volume
- ***Arrhenius relation*** of the diffusion coefficients: $D = D_o exp(-c^{act} B \Omega / k_B T)$
- ***Activation entropy***: $S^{act} = -\left.\frac{\partial g^{act}}{\partial T}\right]_p = -c^{act}\Omega\left\{\left.\frac{\partial B}{\partial T}\right]_p + \beta B\right\}$
- ***Activation enthalpy***: $h^{act} = g^{act} + T \cdot s^{act} = c^{act}\Omega\left\{B - T\beta B - T\left.\frac{\partial B}{\partial T}\right]_p\right\}$
- ***Activation volume***: $v^{act} = \left.\frac{\partial g^{act}}{\partial P}\right]_T = c^{act}\Omega\left\{\left.\frac{\partial B}{\partial P}\right]_T - 1\right\}$

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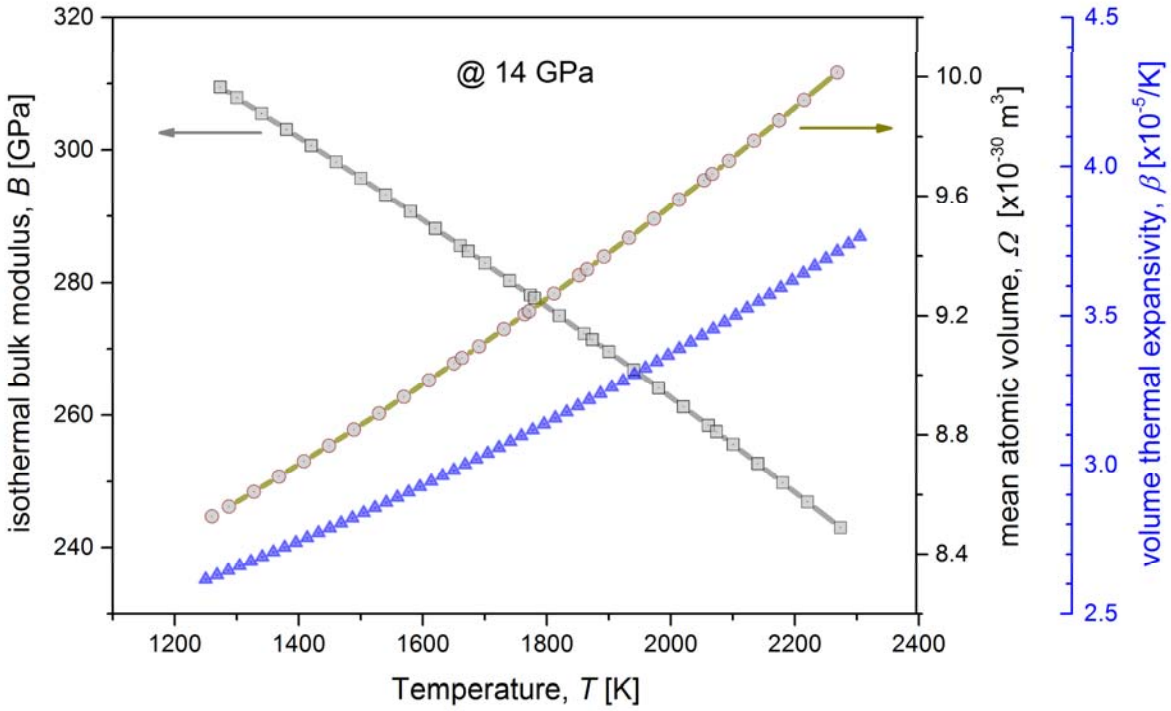
Thermoelastic properties of stishovite



Isothermal bulk modulus B, mean atomic volume Ω and volume thermal expansivity β, at 14 GPa, in the temperature range 1000–2000 °C, were calculated on the basis of the P-V-T EOS of stishovite reported by Wang *et al*. [*J. Geophys. Res*. 2012, *117*, B06209]

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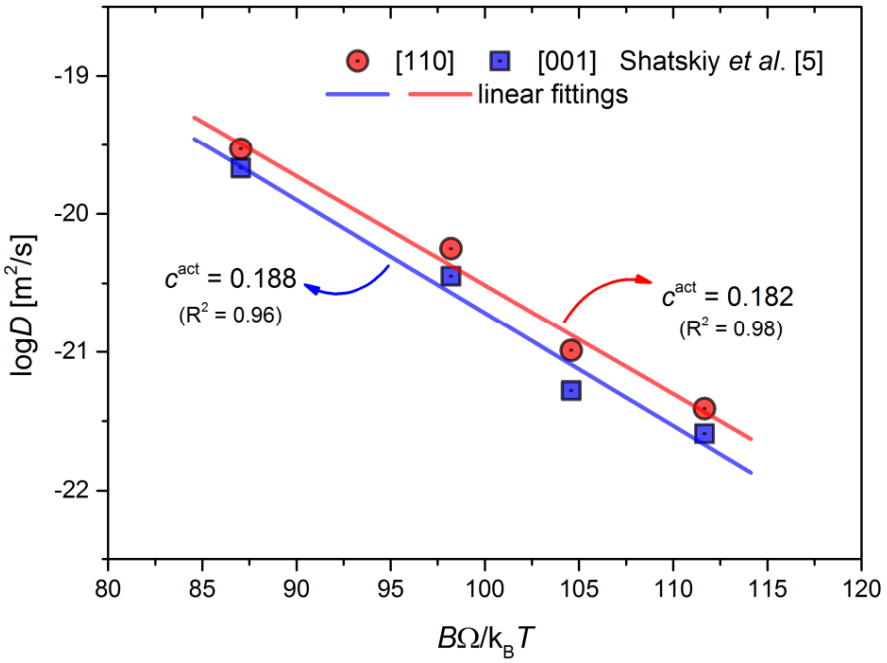
Results and Discussion



Experimental diffusion coefficients of Si in stishovite for the two crystallographic directions, [110] and [001] reported by by Shatskiy *et al.* [*Am. Mineral*. 2010, 95, 135–43], as a function of the dimensionless quantity $B\Omega/k_BT$.

$$lnD = lnD_o - c^{act}\frac{B\Omega}{k_BT}$$

- ✓ The linear dependence of experimental lnD versus $B\Omega/k_BT$ suggests the validity of the $cB\Omega$ model with respect to a single diffusion mechanism.
- ✓ Parameter c^{act} is calculated from the slope of the linear fit.

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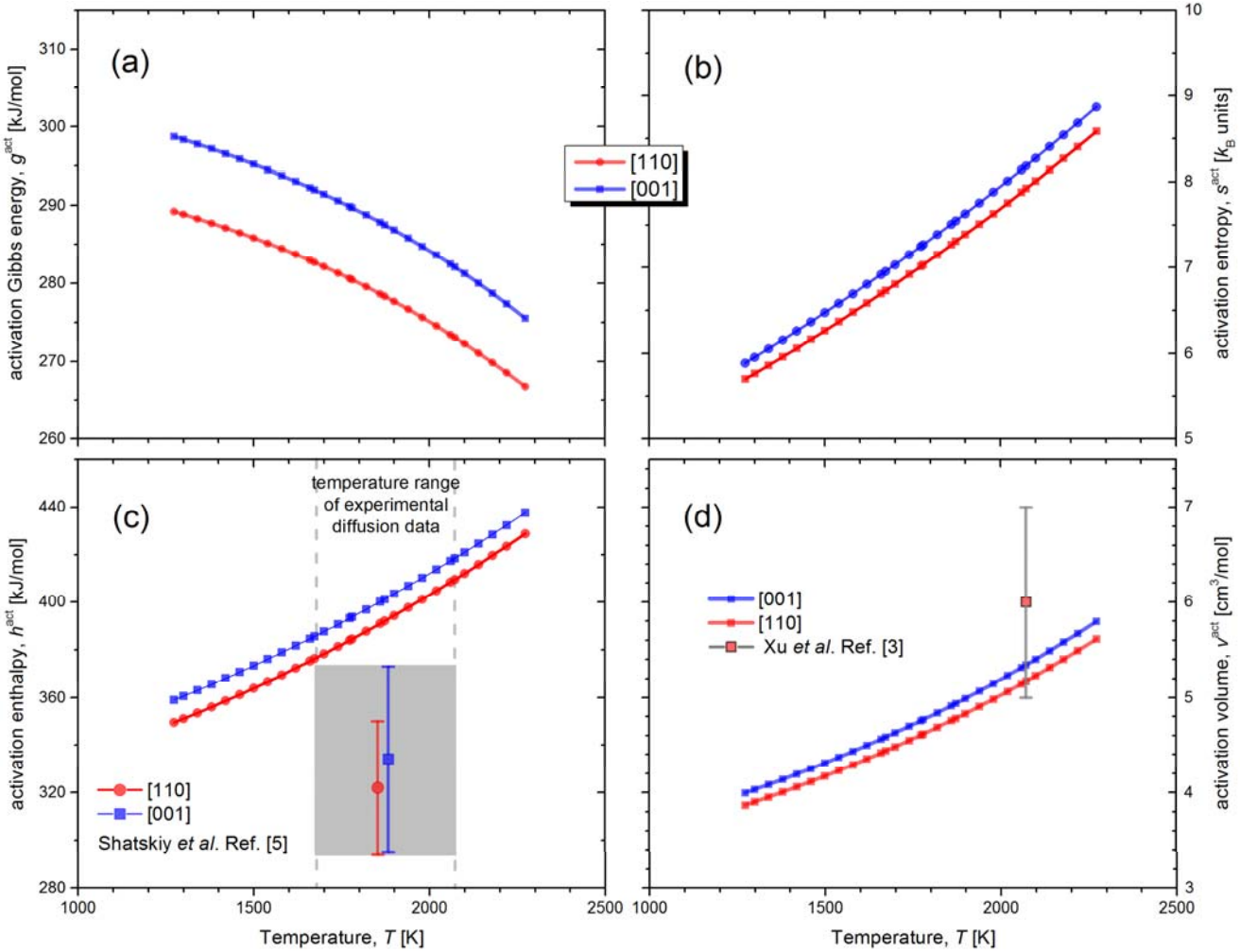
Results and Discussion



Calculated point defect parameters of Si self-diffusion across the [110] and [001] crystallographic directions in stishovite (a) Activation Gibbs free energy, (b) Activation entropy, (c) Activation enthalpy, and (d) Activation volume.

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Results and Discussion

Table. Calculated values of c^{act}, activation enthalpy, activation entropy, activation Gibbs free energy and activation volume for Si diffusion in stishovite. Reported experimental values of activation enthalpy and activation volume are also included.

direction	c^{act}	h^{act} (kJ/mol) calculated	h^{act} (kJ/mol) experimental	s^{act} (k_B units)	g^{act} (kJ/mol)	v^{act} (cm^3/mol) calculated	v^{act} (cm^3/mol) experimental
[110]	0.182 ± 0.016	(350-429) ± 19	322 ± 28 [1]	(5.7-8.6) ± 0.3	(289-267) ± 17	(3.9-5.6) ± 0.6	6.0 ± 1.0 [2]
[001]	0.188 ± 0.021	(359-438) ± 21	334 ± 39 [1]	(5.9-8.9) ± 0.3	(299-276) ± 17	(4.0-5.8) ± 0.6	-

[1] Shatskiy *et al.*, *Am. Mineral*. 2010, 95, 135–43

[2] Xu *et al.*, *Earth Planet. Sci. Lett*. 2017, 459, 332–9

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Conclusions

- ✓ The calculated activation parameters of diffusion, i.e., activation Gibbs free energy, activation entropy, activation enthalpy and activation volume follow a monotonic temperature dependence, which is attributed to the anharmonic behavior of the bulk properties of stishovite.

- ✓ The estimated activation volumes (4.4-5.3 cm^3/mol, in the range 1400-1800 ^oC) are in agreement with reported experimental results. Their values are close to the mean atomic volume which is compatible with vacancy-mediated self-diffusion in stishovite.

- ✓ The theoretical investigation of self- and hetero-diffusion in minerals is feasible on the basis of the $cB\Omega$ thermodynamic model, in order to overcome the experimental difficulties and the lack of experimental diffusion data under high-P and high-T conditions.

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