Diffusion of helium in quartz and coesite: A first-principles study

Shuchen Li[1], Hong Liu[1,*], YaoChun Yang[2], Jianhua Ding[2], Kexin Sun[2], Lei Liu[1],
Li Yi[1], Ying Li[1], Jianguo Du[1], and Jijun Zhao[2]

1. CEA Key Laboratory of Earthquake Forecasting (Institute of Earthquake Forecasting), China Earthquake Administration (CEA)
2. Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education

1 Introduction

Helium gas was often employed to trace useful information in many aspects. For instance, $^3He/^4He$ ratios can reflect the transport of mantle volatiles through the crust in a variety of tectonic environments and provide evidence coupling the leaking mantle to earthquake (Hilton and Porcelli, 2014; Hilton, 2007; Zhou et al., 2017).

The details of the helium gas reserving in mantle and transportation from deep mantle to the exosphere are still limited. To better understand the dynamic and geochemical processes, the diffusion mechanism and rate of diffusion of helium in mantle minerals with pressure should be well constrained. Determinations of diffusivities of He in minerals and melts with high pressure provided constraints on whether He is retained in particular mineral and melts phase after its production, or loss due to heating events and other dynamic process (Cherniak et al., 2014). Although there was much work on the diffusion of helium in minerals, detailed diffusion behaviors of helium gas in minerals have not been well characterized.

This paper discussed helium incorporation and diffusion pathways in perfect crystals of quartz and coesite. The diffusion pathways, activation energies (E_a), and frequencies of helium under the crust and mantle condition were calculated by the first-principles methods.

2 Methods

First-principles calculations were performed using density functional theory (DFT) and the planewave pseudopotential technique in the Vienna *Ab initio* Simulation Package (VASP) (Kresse et al., 1996; Kresse and Hafner, 1993).

The diffusion barriers were determined using climbing-image nudged elastic band (CI-NEB) method (Henkelman, 2000). The diffusion rate is assumed to follow an Arrhenius form: $D = D_0 \exp(-E_a / RT)$ and the diffusion rate is related to the atom vibration by: $D_0 = 1/2\ l^2 v$.
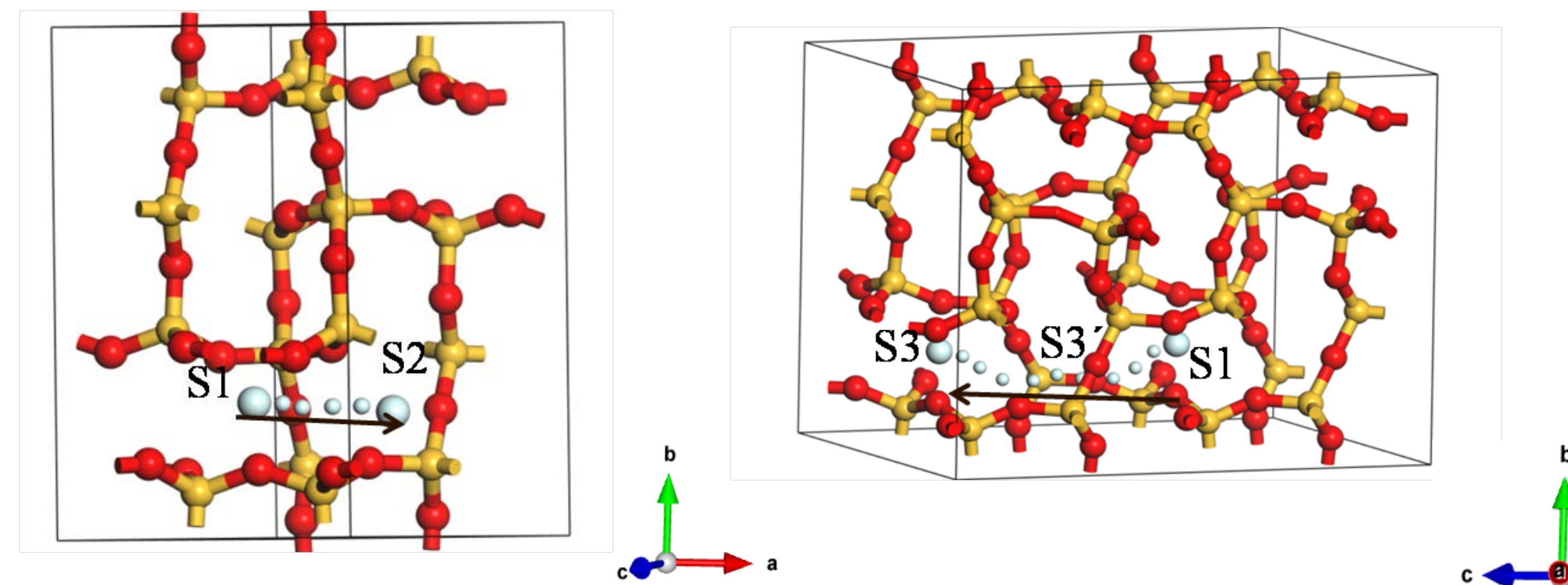
3 Results

Table 1. Formation energies (E_{He}) of single He impurity in quartz and coesite solid compared to previous theoretical values (Lin et al., 2016).

Formation energy (eV)	This work	Lin et al. (2016)
Quartz	0.51	0.52-0.53
Coesite	1.03	\
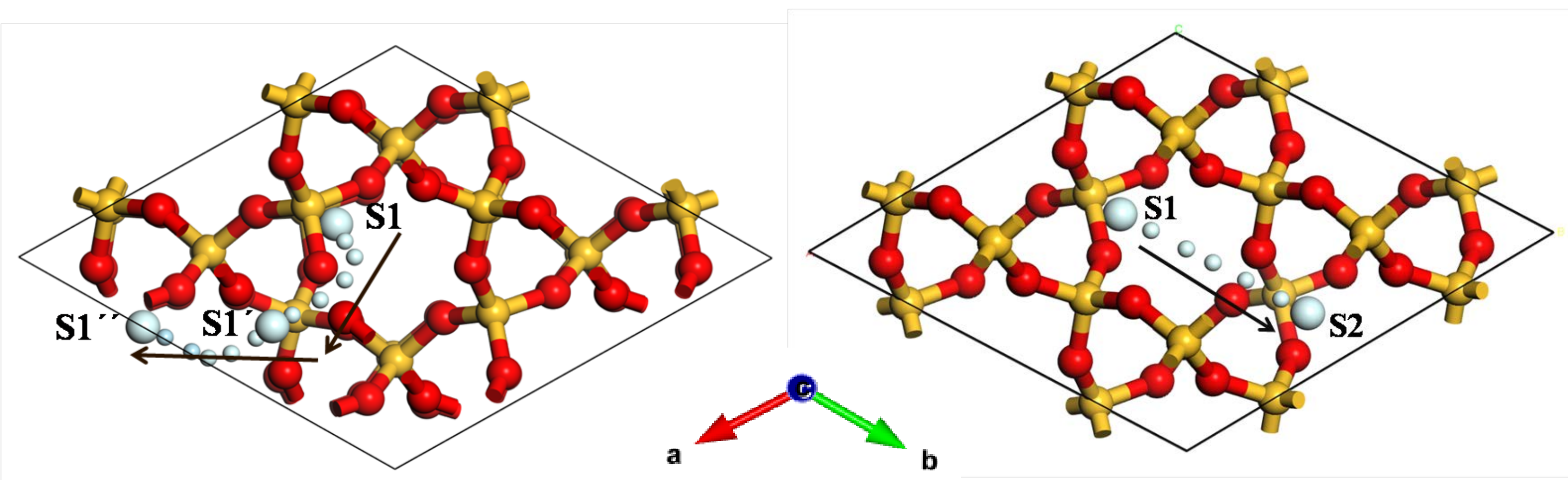
Fig. 1. Diffusion pathways of helium atom in quartz along [010] via the S1′ site and reaching the S1″ site and along [100] reaching the S2 site.

Fig. 2. Diffusion pathways of helium atom in coesite along [100] reaching the S2 site and along [001] via the S3′ site and reaching the S3 site.

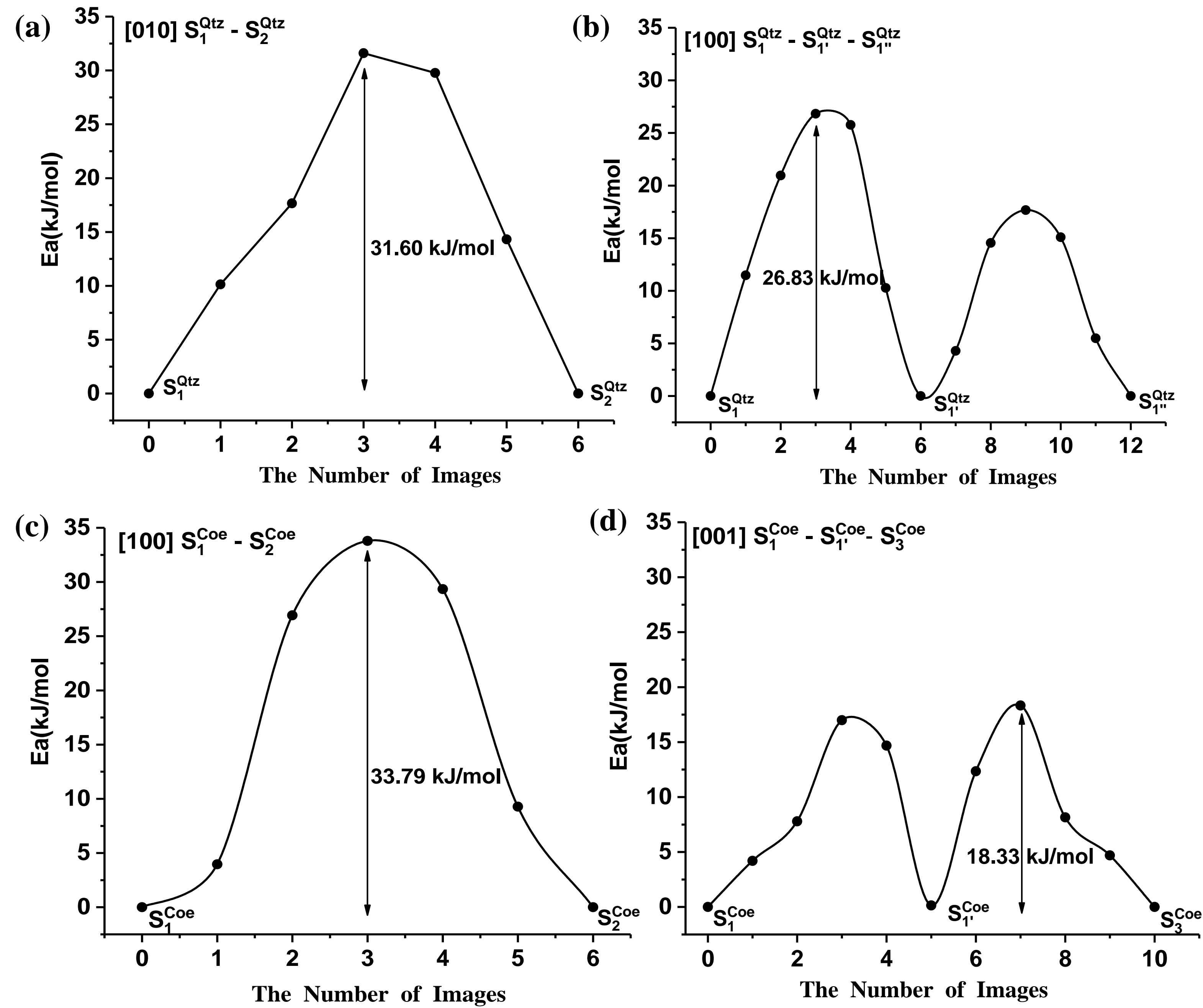The temperature-dependent diffusion coefficients of helium in quartz at ambient pressure can be written as follows:

$D[100] = 1.24 \times 10^{-6} \exp(-26.83\ kJ / mol / RT)\ m^2/s$
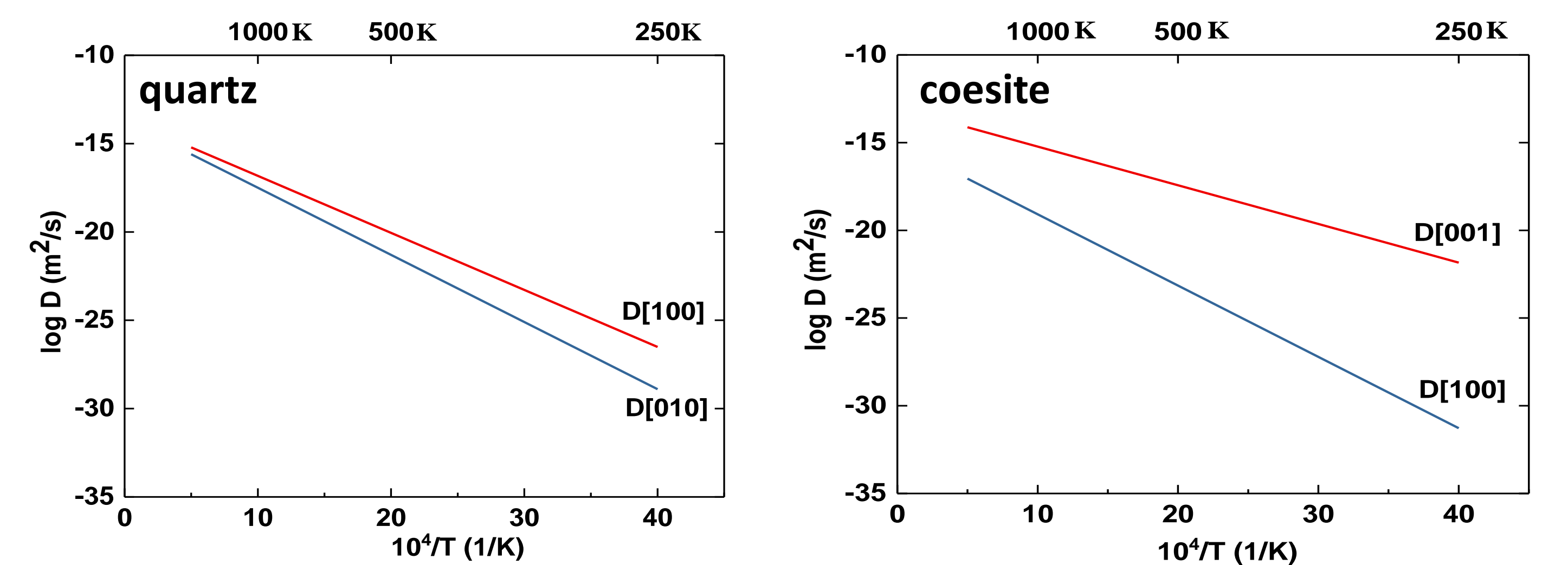$D[010] = 1.11 \times 10^{-6} \exp(-31.60\ kJ / mol / RT)\ m^2/s$

and in coesite:

$D[100] = 3.00 \times 10^{-7} \exp(-33.79\ kJ / mol / RT)\ m^2/s$
$D[001] = 2.21 \times 10^{-6} \exp(-18.33\ kJ / mol / RT)\ m^2/s$

Fig. 3. Energy barriers of different paths for helium diffusion in quartz: (a) S_1^{Qtz}-S_2^{Qtz} path in the [010] direction, (b) S_1^{Qtz} - $S_{1'}^{Qtz}$ - $S_{1''}^{Qtz}$ path in the [100] direction; in coesite: (c) S_1^{Coe}-S_2^{Coe} path in the [100] direction and (d) S_1^{Coe}- $S_{1'}^{Coe}$ -S_3^{Coe} path in the [001] direction.

Fig. 4. Diffusivities as a function of temperature for He in quartz in [100] and [010] directions, and coesite in [100] and [001] directions.
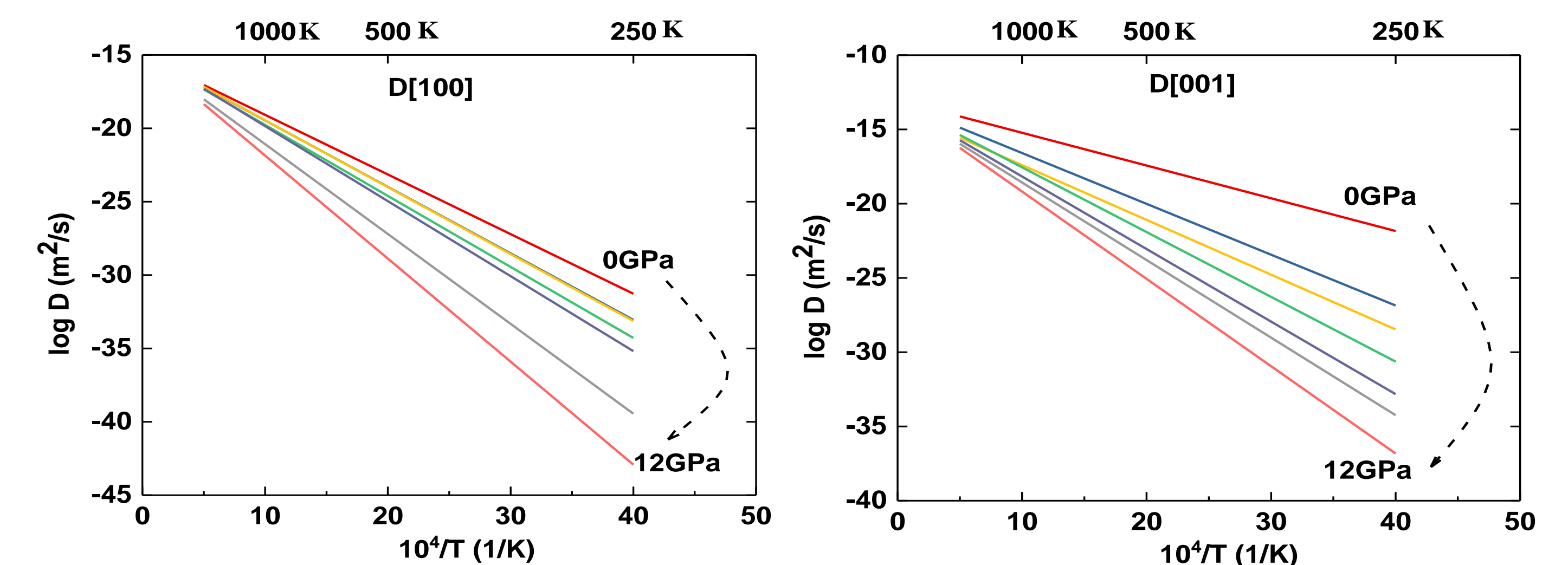
Fig. 5. Effect of pressure on helium diffusion in coesite up to 12 GPa in the [100] and [001] directions.

5 Conclusion

1. The computed formation energies E_{He} of 1.03 eV for the most energetically favorable site in coesite is considerably higher than in quartz ($E_{He} = 0.51$ eV). The difference may be due to the more spacious space for the He interstitial and greater He-O nearest distance in quartz.

2. Diffusion in the *a*-axis ([100] direction) is the most energetically favorable directions ($E_a[001] = 26.83$ kJ/mol) in quartz. However, diffusion in c-axis ([001] direction) is the most favorite direction ($E_a[001] = 18.33$ kJ/mol) in coesite. Helium diffusion in ideal coesite is greater than in ideal quartz and the degree of anisotropy is much more pronounced in coesite.

3. Helium diffusion in coesite is significantly pressure-dependent at low temperature. When the pressure reached up to 12 GPa, the activation energies increased with the pressure and the diffusion for [001] is higher than [100] at any pressure.