

# An experiment study of quartz-coesite transition at differential stress

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**Abstract** In order to study quartz-coesite transition under the conditions of differential stress, experiments of quartzite deformation were carried out using a triaxial testing system with a Griggs type solid medium pressure vessel. Analyses on the plastically-deformed samples under optical microscope and Raman spectra show that fine-grained coesite was present in the region of samples adjacent to the pistons at temperatures of 950—1000°C, confining pressure of 1.3 GPa, differential stress of 1.5—1.67 GPa, and total strain of 75%—81%. It is evident that the transition pressure of quartz-coesite at differential stress and intensely-strained conditions is far lower than the pressure for coesite stability at isostatic pressure. In other words, the stress condition of coesite occurrence is not unique. The decrease in confining pressure for quartz-coesite transition under differential stress conditions is controlled by a combined effect of the maximum principal stress that provides a high stress environment, and differential stress that causes sample deformation. Coesite was produced in the plastically-deformed samples in this study, but it can occur in both semi-brittle and plastic deformation regimes as seen in previous studies. Phase transition in semi-brittle deformation regime is caused by local mechanical instability induced by shear deformation, and phase transition in plastic flow regime is due to strain instability induced by the presence of a high dislocation density within intensely-deformed quartz crystals.

**Keywords:** quartz-coesite transition, differential stress, high temperature, high pressure.

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Coesite, a high pressure phase of SiO<sub>2</sub>, was originally synthesized at laboratory by Coes<sup>[1]</sup>. A lot of experiments of quartz-coesite transition have been made at isostatic pressures since then, and equations for transition pressure as a function of temperature have been established according to these results<sup>[2—8]</sup>. All of the experiments indicate that the pressure for stable coesite is greater than 2 GPa in a temperature rang of 300—1700°C. Coesite is now often used for calibrating the pressure of solid medium pressure vessel as quartz is easy to transform to coesite and the transition pressure is reproducible under high isostatic pressure<sup>[9]</sup>. Natural coesite was first found from Meteor aerolite crater in Arizona by Chao and

his colleague<sup>[10]</sup>. Later, coesite was found at several ultrahigh-pressure metamorphic belts in the world<sup>[11]</sup>. As one of diagnostic ultrahigh-pressure metamorphic minerals, coesite is generally used to determine the peak metamorphic pressure. In order to investigate quartz-coesite transition condition in coesite-bearing eclogite, some studies were made via experiments on the effect of loading path, temperature and time to quartz-coesite transition at high pressure (greater than 3 GPa)<sup>[12]</sup>, tests to establish steady state flow laws of coesite<sup>[13]</sup>, and acquisition of activation energy for transition from coesite to quartz, which was found to be 242—269 kJ/mol<sup>[14]</sup>. However, it was also found that coesite is present in deformed quartz sample at confining pressure of 1—2 GPa in the experiments of studying brittle-plastic transition and recrystallization of quartz<sup>[15—18]</sup>. The transition pressure is far from the stable field of coesite at isostatic pressure (greater than 2 GPa). The fact that the pressure for quartz-coesite transition under differential stress is lower than that at isostatic pressure implies that the pressure for coesite formation is not an unique function of temperature<sup>[19—21]</sup>. With these in mind, it is of great interest to study the conditions for coesite formation under different types of stress state. In this paper, we report new experimental results of quartz-coesite transition at differential stress.

## 1 Experimental condition, method and samples

All the experiments were performed in a triaxial testing system with a Griggs type solid medium pressure vessel at Institute of Geology, State Key Laboratory of Earthquake Dynamics, China Earthquake Administration. The detailed description about the testing system is given in a previous paper<sup>[22]</sup>. The experimental temperature was 900—1020°C, and confining pressure was 1.2—1.4 GPa. Before applying the differential stress, first the axial and confining pressures were applied with a pre-calibrated proportion to the set point of isostatic pressure. When the pressures reached a given value, the axial pressure was switched to constant load control. Then temperature is applied with heating rate of 10°C/min at the beginning, and switches over to 5°C/min when getting closed to the set point. 10 min waiting is made after the temperature reaches the final value, and then the confining pressure is adjusted to the set point. The axial stress is applied at constant strain rate of  $2.5 \times 10^{-4}$ — $5 \times 10^{-5}$  s<sup>-1</sup> with confining pressure and temperature fixed. At the end of test, turn off heating power to quench the sample, and unload both confining and axial pressures quickly. The samples are natural quartzite collected from Great Wall series, with fine-grained texture and no evident anisotropy, in which the content of quartz is more than 99% and very small amount muscovite and plagioclase can be seen. The average grain sizes of quartz are 0.08—0.12 mm, and local undulance extinction in quartz grains can be seen under crossed polarizer.

## 2 Experimental results

In the highly-deformed samples, grains with little sign of plastic deformation appeared adjacent to two ends of the sample. These grains are identified as biaxial crystals under optical microscope (Fig. 1). The grains are further identified with laser Raman spectrometer at School of Geoscience and Space Sciences, Peking University and Institute of Geology, Chinese Academy of Geological Sciences. Typical laser Raman spectra of coesite (Fig. 2) were found in the ends of two experimental samples (Q39 and Q49) which were tested at School of Geoscience and Space Sciences, Peking University. Quartz was often partly transformed towards coesite as manifested by coexistence of strong bands of coesite and weak bands of quartz in typical coesite Raman spectra, as well as coexistence of strong bands of quartz and weak bands of coesite in typical quartz Raman spectra. The similar coexistence bands of coesite and quartz in Raman spectra were also reported in natural samples<sup>[23]</sup>.

The conditions under which coesite appeared in deformed samples are shown in Table 1. The confining pressure is 1.3 GPa, temperature is 950–1000°C, maximum principal stress ranges from 2.8 to 3.0 GPa, hence differential stress is 1.5–1.67 GPa. Maximum strain reaches to 75%–81%. Deformation of all these samples is in the plastic regime. The conditions of these experiments in common are large strain and low confining pressure. Axial load in sample of Q39 is applied initially by constant strain rate control and switched to constant load control when axial stress comes close to the yield stress. A

pronounced phenomenon is that the strain-time relation under constant load once showed acceleration and then turned to very slow strain rate (Fig. 3(a)). In sample Q49, constant strain rate control is applied in the whole deformation process. In this sample, there is a sudden stress drop when the strain is around 70%, then the stress raises a small amount (Fig. 3(b)). These phenomena are likely the results of volume change of grains because of phase transition from quartz to coesite. The densities of quartz and coesite are 2.65 g·cm<sup>-3</sup> and 2.91–2.92 g·cm<sup>-3</sup> respectively, and the activation volume of quartz and coesite are respectively 20.592 and 22.688 cm<sup>3</sup>·mol<sup>-1</sup><sup>[12,13]</sup>. The volume contraction of grains during phase transition from quartz to coesite is about 8.82% according to these data. For example, in sample Q49, assume that the coesite region is laterally extended in the sample and connected with its surroundings in series. According to Hooke's law for elasticity, we can calculate stress drop due to volume contraction during phase transition from quartz to coesite.

$$\Delta\sigma = \lambda E\Delta\varepsilon_v + 2G\Delta\varepsilon_x, \quad (1)$$

where

$$\lambda = \frac{\nu}{(1+\nu)(1-2\nu)}, \quad (2)$$

$$G = \frac{E}{2(1+\nu)}, \quad (3)$$

$$\varepsilon_v = \frac{\Delta V}{V}, \quad (4)$$

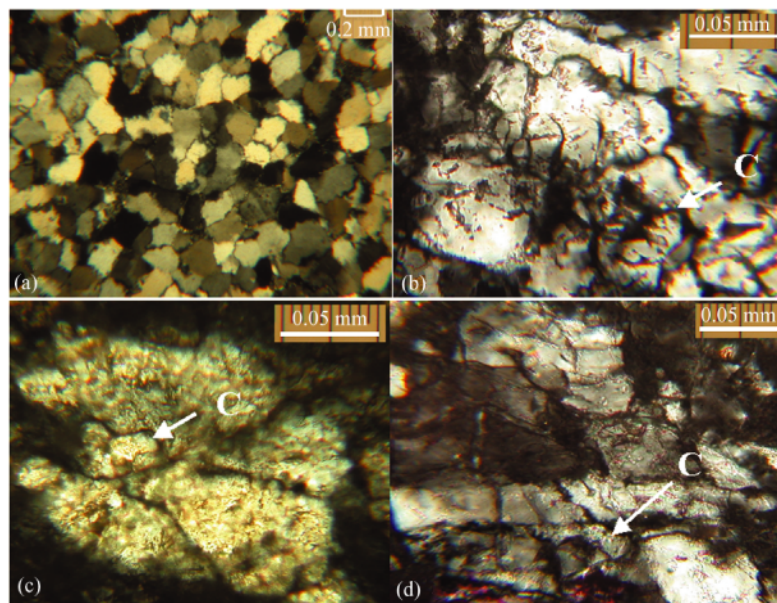


Fig. 1. The microstructure of experimental samples. (a) The starting samples; (b) the position where coesite bands appeared in Raman spectra testing at sample Q39; (c) and (d) the position where coesite bands appeared in Raman spectra testing at sample Q49. All crossed nicols.

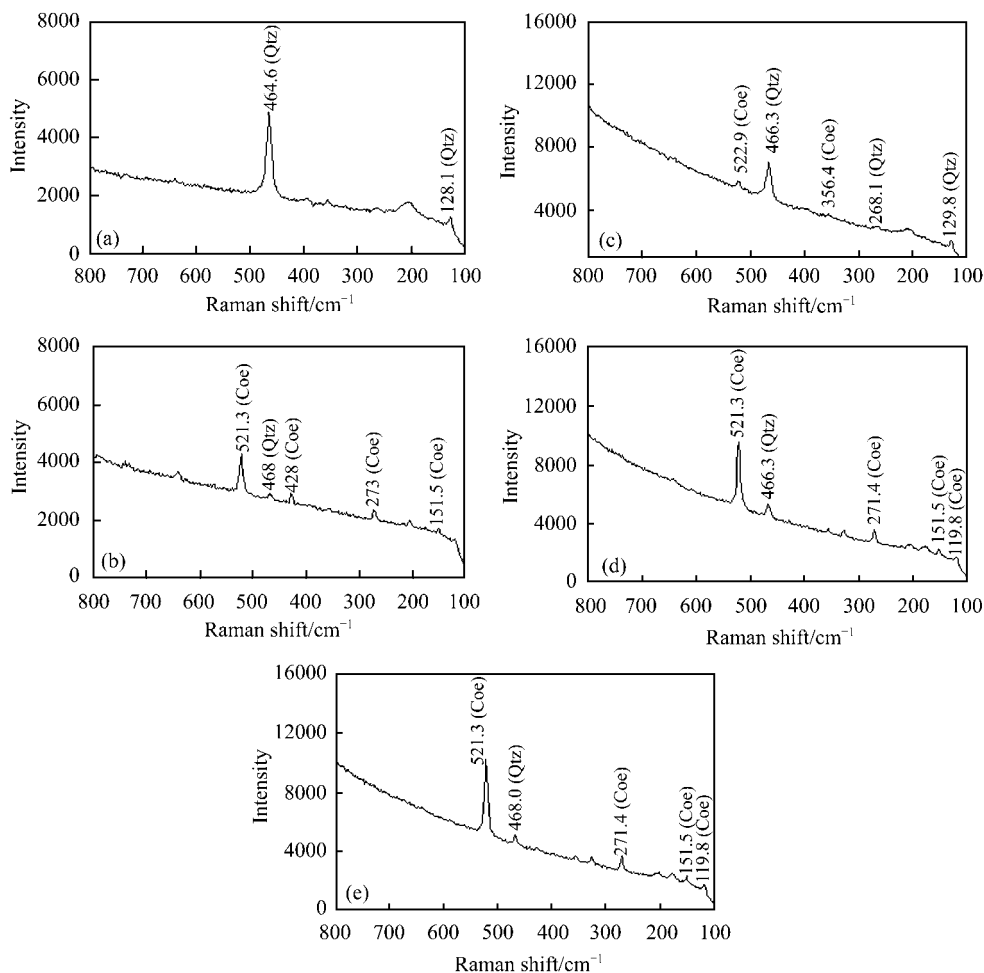


Fig. 2. The typical Raman spectra of quartz and coesite in experimental samples. All Raman spectra presented here were performed at Peking University. (a) The quartz spectra of deformed sample Q39; (b) coexistence of strong bands of coesite (Coe) and weak bands of quartz (Qtz) in typical coesite Raman spectra of sample Q39; (c) coexistence of strong bands of quartz (Qtz) and weak bands of coesite (Coe) in typical quartz Raman spectra of sample Q49; (d) and (e) coexistence of strong bands of coesite (Coe) and weak bands of quartz (Qtz) in typical coesite Raman spectra of sample Q49.

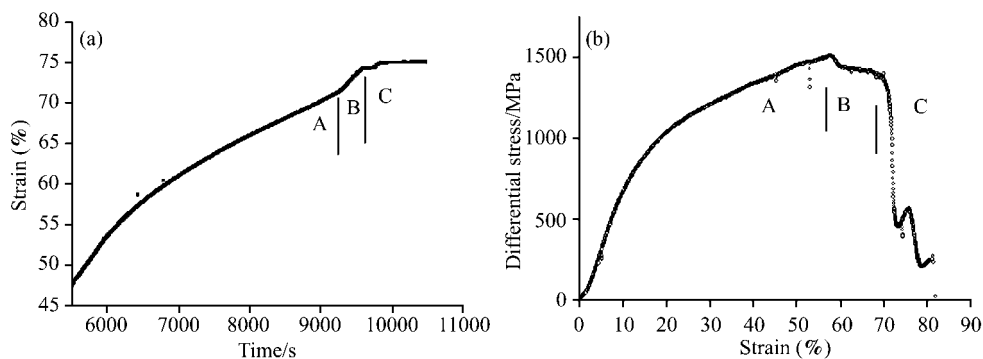


Fig. 3. The stress curves of experiments in which coesite was observed. (a) The strain versus time curve of constant load controlling experiment (Q39). A, Segment-stable creep; B, segment-accelerated creep; C, segment-slow creep. (b) The stress versus strain curve of constant strain rate controlling experiment (Q49). A, Segment-stable creep; B, segment-increased temperature from 980 to 1000°C; C, segment-stress dropped sudden.

$$\varepsilon_x = \frac{\varepsilon_v}{3}, \quad (5)$$

$$\Delta\sigma = \Delta\varepsilon_v \left[ \frac{\nu E}{(1+\nu)(1-2\nu)} + \frac{E}{3(1+\nu)} \right]. \quad (6)$$

The volume change during quartz-coesite transition is

$$\Delta\varepsilon_v = 8.82\% \text{ (Renner et al., 1997, 2001)}$$

and for Poisson's ratio  $\nu = 0.25$  and elastic modulus of experiment Q49  $E = 9.37 \times 10^3$  MPa,

$$\Delta\sigma \approx 550 \text{ MPa.}$$

The calculated stress drop due to volume contraction during phase transition from quartz to coesite turned out to be 550 MPa, and the actual stress drop in the experiment is larger than this value. This phenomenon of volume contraction during phase transition from quartz to coesite was not reported in previous studies<sup>[15–18]</sup>.

Obviously, the confining pressure for coesite formation under differential stress is lower than the isostatic pressure beyond which coesite is stable, i.e. the phase boundary of quartz-coesite transition moves toward lower pressure under differential stress condition. The phase transition mechanisms of quartz are different between

intensely-deformed condition and isostatic pressure condition. In other words, the formation condition of coesite is not unique.

### 3 Discussion and conclusion

The mechanical data (Table 1) for samples in which coesite formed are plotted on SiO<sub>2</sub> phase diagram which was obtained according to experimental results under isostatic pressure (Fig. 4). The confining pressure (Fig. 4(a)), differential stress (Fig. 4(c)) and mean stress (Fig. 4(d)) plotted against temperature are all below stable field for coesite, i.e. all of the samples containing coesite were deformed in pressure region for stable quartz. However, the maximum principal stress plotted against temperature for these samples all lay around the boundary of quartz-coesite transition (Fig. 4(b)). Here, confining pressure is the minimum principal stress, and the maximum principal stress is the difference between apparent axial pressure and friction, differential stress is the difference between maximum principal stress and confining pressure, and mean stress is the average of the three principal stresses. The differential stress given in this study is the peak differential stress that the rock samples can support, i.e. the strength at a given condition.

Table 1 The experimental conditions of coesite occurrence under differential stress

Samples No.	Temperature/°C	Confining pressure/GPa	Differential stress/GPa	Maximum main stress/GPa	Mean stress/GPa	Strain (%)	The region where coesite presents
Q39	950	1.3	1.67	3.0	1.9	75	coesite appears at the ends of samples adjacent to the piston
Q49	980–1000	1.3	1.50	2.8	1.8	81	

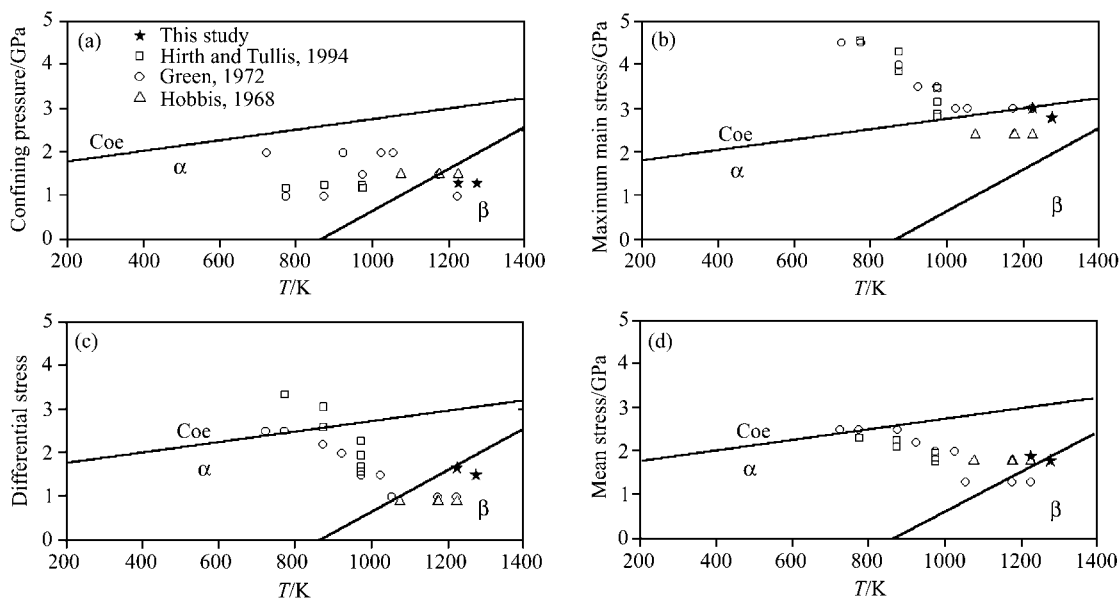


Fig. 4. Pressure and stress versus temperature plots showing the conditions, where coesite appeared under differential stress. Coe,  $\alpha$ ,  $\beta$  is the stability field of coesite,  $\alpha$ -quartz,  $\beta$ -quartz under isostatic pressure. The  $\alpha$ -quartz-coesite phase transition boundary is from Kitahara and Kennedy<sup>[4]</sup>, the  $\alpha$ - $\beta$  quartz transition boundary is from Cohen and Klement<sup>[5]</sup>. The symbols of pentagram, square, circle, and triangle are the results of this study, and refs. [15,17,18].

Previous experimentalists found coesite appeared in deformed quartz sample at confining pressure of 1–2 GPa when they studied brittle-plastic transition and recrystallization of quartz<sup>[15–18]</sup>. The confining pressure in this work was lower than the isostatic pressure for stable coesite. As the major focuses of the published papers were on quartz deformation, they just reported the formation of coesite in samples<sup>[15]</sup>, and analyzed the cause of its formation<sup>[17,18]</sup>, but did not document the detail of experimental phenomenon about quartz-coesite transition in the papers. As seen in Fig. 4, the conditions of confining pressure, stresses and the feature of intense plastic deformation under which coesite appeared in this study are similar to the results of Hobbs's experiments<sup>[15]</sup> and Green's high temperature (higher than 700°C) experiments<sup>[16,17]</sup>. Confining pressure, differential stress and mean stress are below quartz-coesite transition boundary in SiO<sub>2</sub> phase diagram, but maximum principal stress is near the transition boundary. In addition, coesite appeared at the ends of intensely-deformed samples, and quartz around coesite has experienced intense plastic deformation. Green<sup>[17]</sup> suggested that coesite occurrence in lower confining pressure is due to the high dislocation density of quartz in intensely-deformed samples. The conditions of stress and deformation under which coesite grew in plastically-deformed samples are different from those in semi-brittle deformation regimes at lower temperature (400–700°C) as reported by Green<sup>[16,17]</sup> and Hirth and Tullis<sup>[18]</sup>. In semi-brittle deformation regimes, all of the samples containing coesite were deformed at confining pressure below coesite stability boundary, and differential stress and mean stress lies around the isostatic transition boundary of quartz-coesite, but the maximum principal stress for these samples all lie within coesite stability field. The coesite is present along shear fault zones and along grain boundaries orienting perpendicularly to maximum principal stress, and it is also present in the ends of samples adjacent to the pistons, where quartz around coesite seldom deforms. Hirth and Tullis<sup>[18]</sup> suggested that maximum principal stress likely controls the phase transition.

The common feature of coesite formation under differential stress in both semi-brittle and plastic deformation regimes is that the confining pressure is lower than the coesite stability boundary under isostatic pressure. However, the deformation mechanisms and mechanical conditions under which coesite grew are different in semi-brittle deformation regimes, and differential stress and maximum principal stress under which coesite grew are close to or higher than the pressure of quartz-coesite transition under isostatic pressure, but the strain needed is small. However, in plastic deformation regimes, maximum principal stress and differential stress under which coesite grew are close to or lower than the pressure of quartz-coesite transition under isostatic pressure, but the strain it needed is large.

According to the feature of sample deformation and

the mechanical conditions for coesite formation, we suggest that quartz-coesite transition at lower confining pressure can be controlled by combined effect of maximum principal stress<sup>[18]</sup> and differential stress<sup>[19–21]</sup>. In semi-brittle deformation regimes, the samples are under high stress environment because of high value of maximum principal stress, and there will be stress concentration around macro or micro fractures, which induces mechanical instabilities, and in turn induces localized quartz-coesite phase transition outside the isostatic coesite stability field. In plastic deformation regimes, in addition to the high stress environment due to high maximum principal stress, the high density of dislocations developed in intensely-deformed samples due to the effect of differential stress induces strain instabilities which can result in localized quartz-coesite phase transition outside the coesite stability field<sup>[19–21]</sup>. The high density of dislocations in quartz increases both the normal stress around quartz and the free energy of deformed quartz. If the dislocation density in quartz was to exceed  $10^{12}$  cm<sup>-1</sup>, the free energy of deformed quartz should be greater than that of undeformed coesite<sup>[16,17]</sup>, and quartz would become less stable than coesite, and coesite crystals could nucleate and grow outside its stability field. It is important that quartz-coesite transition occurs only when confining pressure is greater than a certain value (greater than 1 GPa for example) in both semi-brittle and plastic regimes. If the confining pressure is too small, the phase transition cannot occur no matter how much the differential stress is.

The conditions of pressure and stress as well as the feature of intense plastic deformation of samples under which coesite appeared in this study are similar to the results of Hobbs's experiments<sup>[15]</sup> and Green's high temperature experiments<sup>[16,17]</sup>, but are different from the results in semi-brittle deformation regimes at lower temperature (400–700°C) reported by Green<sup>[16,17]</sup> and Hirth and Tullis<sup>[18]</sup>. We suggest that the mechanisms responsible for the two types of phase transition are not the same. Although the experimental result is preliminary, it implies that quartz-coesite transition could happen outside its stability field induced by mechanical instability (semi-brittle) or strain instability (due to intense plastic deformation). The necessary condition for quartz-coesite transition at confining pressure is that the rocks have enough strength to support both high maximum principal stress and differential stress and form high stress environment or compression/shearing environment in samples. The results presented here about coesite occurrence outside the stability field indicate that the condition for coesite nucleation and growing is not unique, hence extreme care should be exercised in estimating the pressure according to appearance of the typical mineral coesite as the pressure symbol in both laboratory and natural environment, especially when shear deformation happens in-depth analyses on the physics of the phase transition process are necessary.

It is not adequate to estimate the forming pressure of ultra-high-pressure rocks only according to the results of this study because the experimental conditions are so different from the forming condition of ultra-high-pressure rocks. In discussion on effects of differential stress in forming ultrahigh-pressure rocks two questions should be focused on, namely, whether the ultrahigh-pressure rocks were formed in tectonic environment with differential stress, and how much the greatest differential stress that the ultra-high-pressure rocks could support was. So we suggest that one of the possible solutions of these questions lies on the study of rheological properties of minerals and rocks relevant to the ultra-high-pressure rocks.

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